Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Ultrafast spectroscopy on water-processable PCBM: rod-coil block copolymer nanoparticles

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1. Synthesis of the block copolymers BCP2 and BCP100

The two monomers used for the synthesis of the rod blocks of BCP2 and BCP100 were purchased from Lumtec-Luminescence Technology Corp, and used as received without further purification. Whereas, 2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO radical) was purchased from Sigma-Aldrich, handle under nitrogen atmosphere, and used for the synthesis of brominated tert-butyl isopropyl phenyl nitroxide (TIPNO-PhBr) as previously reported[1]. Styrene, 4-vyilpyridine (4VP), and anisole were used for the coil block preparation, as well as all the solvents used for the chemical reactions were dried by standard procedures, and stored at -20 °C under nitrogen atmosphere.

Nuclear Magnetic Resonance (NMR) spectra were recorded by a Bruker NMR DRX 600 spectrometer (600 MHz), using 1,2-dideutero-1,1,2,2-tetrachloroethane (TCE-d2) as solvent at 313 K.

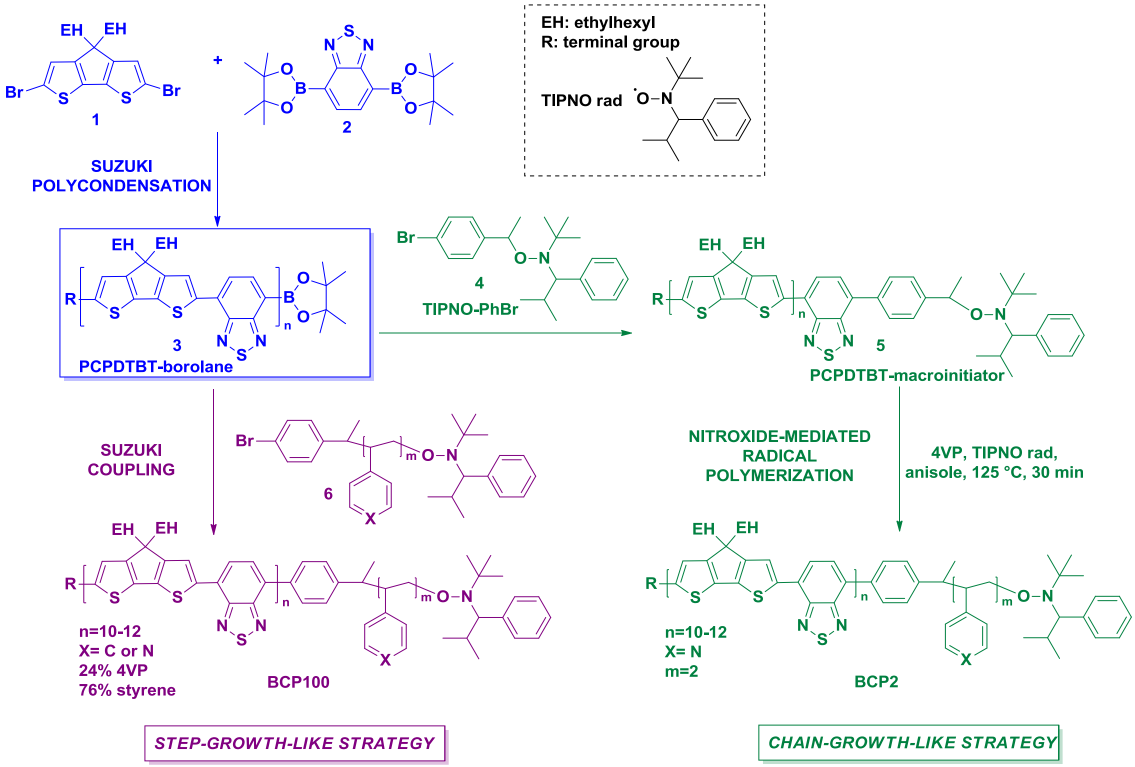
Size Exclusion Chromatography (SEC) measurements were performed with an integrated GPCV2000 SEC system from Waters with two on-line detectors (differential viscometer DV and a differential refractometer DRI), using some polystyrene (PS) standards with narrow molar mass distribution (MMD) as universal calibration of the SEC-DV chromatographic system.

In the case of **BCP2**, the MMD of the macroinitiator **5** was determined using THF+0.25% TBAB as the eluent, column set 2 PLGel Mixed C PL with a flow rate 0.8 ml/min at 35 °C.

The relative average coil block lengths were determined by comparing the normalized integral of the signal at 6.4 ppm corresponding to 2 aromatic protons of 4VP and the normalized integral of the signal at 7.9 ppm corresponding to 2 aromatic protons of cyclopentadithiophene residue into the rod block, with 4VP unit Mw=105 u.m.a[2].

In the case of **BCP100**, the MMD of the rod-coil block copolymer was determined using a mixture of THF:DMF (80:20) as the eluent, column set 3 PLgel (2 Mixed C+100Å) PL with a flow rate 0.8 ml/min at 35 °C.

Two different strategies were used for the synthesis of the block copolymers BCP2 and BCP100 that are reported in Scheme S1.



Scheme S1. Synthetic routes for the preparation of the rod-coil block copolymers in this work, BCP2 with a coil block of 2 repeating units of 4VP, and BCP100 with a random P(S-*r*-4VP) coil block with 24 % 4VP.

Synthesis of the macromer (3). The macromer was synthetized through a Suzuki polycondensation as already reported[2].

In brief, the two monomers **1** and **2** (Scheme 1) were introduced into a Schlenk tube in equimolar ratio and undergone to three vacuum/nitrogen cycles. Then they were dissolved into freshly-distilled THF. Then, K_2CO_3 aq. 4 M (10 eq) and Aliquat 336 were added. Finally, the catalyst $Pd_2(dba)_3$ (1%eq) and $P(p\text{-tol})_3$ (4%eq) were separately prepared and added to the reaction mixture, that was then heated at 70 °C for 8 h. Therefore, for the capping of the polymeric chain 5-methylthiophene-2-boronic acid pinacol ester (3 eq) was added to polycondensation, allowing for stirring overnight.

Thus, heating was stopped and the mixture was filtered through Celite® to remove the catalyst. The recovered filtrate was concentrated in vacuo and then poured into methanol and recovered through filtration. The product was extracted in Soxhlet apparatus (using sequentially acetone, ethyl acetate, chloroform) and the chloroform extract was used for the subsequent preparations.

1H-NMR (TCE-d2, 600 MHz, ppm) δ: 8.5 (br, 2H, phenyl); 8.0 (br, 2H, thienyl), 2.0 (br, 4H, CH_2 alkyl chain), 1.1-0.9 (br, 18H, CH and CH_2 alkyl chain), 0.8-0.5 (br, 12H, CH_3 alkyl chain). Mn=7.9 KDa, Mw/Mn=1.4.

Synthesis of the macroinitiator (5). The same procedure used for the synthesis of **3** (Scheme S1) was performed also for the synthesis of the macroinitiator, but for the capping of the polymeric chain after 8 h was used TIPNO-PhBr (1.5 eq), allowing for stirring for 16 h.

Then, the mixture was cooled and poured into methanol and recovered through filtration twice to achieve a dark blue product (yield 50%). No further purification was performed in order to avoid the de-activation of the TIPNO derivative, and the macroinitiator was directly used for the synthesis of rod-coil block copolymer through the nitroxide-mediated radical polymerization of the 4VP.

1H NMR (TCE-d2, 600 MHz, ppm) δ: 8.1 (br, 2H, PCPDTBT backbone), 7.9 (br, 2H, PCPDTBT backbone), 7.6 (m, 6H, Ph TIPNO), 7.0 (m, 3H, Ph TIPNO), 4.3-3.5 (m, 3H, CH-N, CH-O, CH i-propyl TIPNO), 2.0 (br, 4H, CH_2 alkyl chain PCPDTBT backbone), 1.3-0.9 (br, 18H, CH and CH_2 alkyl chain PCPDTBT backbone), 0.7-0.6 (br, 12H, CH_3 alkyl chain PCPDTBT backbone). Mn=5.4 KDa, Mw/Mn=2.5.

Synthesis of BCP2. For the synthesis of BCP2 was performed through a chain-growth like strategy, starting the radical polymerization of the 4VP from the macroinitiator **5**.

The macroinitiator **5** (Scheme S1), 4VP and radical TIPNO (5% eq) were degassed through freeze-pump-thaw several times and then dissolved into dry anisole, and the mixture was heated at 125 °C under nitrogen atmosphere. The radical polymerization was stopped after 30 minutes through immersion into liquid nitrogen bath. The crude mixture was purified through subsequently pouring and recovering of the solid product into differently selective solvents (hexane and methanol, for the rod-coil block copolymer and for the unreacted macroinitiator respectively).

1H-NMR (TCE-d2, 600 MHz, ppm) δ: 8.3 (br, 2H, 4VP), 8.1 (br, 2H, phenyl PCPDTBT), 7.9 (br, 2H, thienyl PCPDTBT), 7.6 (m, 6H, Ph TIPNO), 7.0 (m, 3H, Ph TIPNO), 6.3 (br, 2H, 4VP), 2.0 (br, 4H, CH_2 alkyl chain PCPDTBT), 1.3-0.7 (br, 18H CH and CH_2 alkyl chain PCPDTBT and 9H CH_3 t-butyl TIPNO), 0.7 (br, 12H CH_3 alkyl chain PCPDTBT and 6H CH_3 i-propyl TIPNO). Mn=5.6 KDa, calculated through 1H-NMR.

Synthesis of BCP100. For the synthesis of BCP100 was performed through a step-growth like strategy, preparing separately the two blocks and then coupling then through a Suzuki reaction.

The random coil block P(S-*r*-4VP) **6** (Scheme S1) was synthesized as reported[3], feeding the nitroxide-mediated radical polymerization with 20 % of distilled 4VP and 80 % of styrene, to achieve an actual 24 % of 4VP random insertion into the growing polymeric chain of styrene, as determined by 1H-NMR[3].

1H NMR (TCE-d2, 600 MHz, ppm) δ: 8.2 (br, 2H, 4VP), 7.0 (br, 3H, Sty), 6.8-6.0 (br, 2H 4VP and 2H styrene), 2.0-0.9 (br, 6H, CH and CH_2 alkyl chain). Mn=13.7 KDa, Mw/Mn=1.4.

The two block **3** and **6** were introduced into a Schlenk tube in equimolar ratio and undergone to three vacuum/nitrogen cycles. Then they were dissolved into dry toluene. Then, K_2CO_3 aq. 1 M (20 eq) and Aliquat 336 were added. Finally, a solution of the catalyst $Pd(PPh_3)_4$ (5%eq) into dry toluene were separately prepared and added to the reaction mixture, that was then heated at 95 °C for 72 h. Thus, heating was stopped and the mixture was cooled at room temperature, diluted with toluene and filtered through Celite® to remove the catalyst. The recovered filtrate was concentrated in vacuo and purified through subsequently pouring and recovering of the solid product into differently selective solvents (methanol and hexane, for the rod-coil block copolymer and for the unreacted macromer, respectively)

1H-NMR (TCE-d_2, 600 MHz, ppm) δ: 8.2 (br, 2H, 4VP), 8.0 (br, 2H, phenyl PCPDTBT), 7.8 (br, 2H, thienyl PCPDTBT), 7.6 (m, 6H, Ph TIPNO), 7.2-6.8 (br, 3H, styrene), 6.7-6.1 (br, 2H 4VP and 2H styrene), 2.0 (br, 4H, CH_2 alkyl chain PCPDTBT), 1.1-0.8 (br, 18H, CH and CH_2 alkyl chain PCPDTBT and 9H CH_3 *t*-butyl TIPNO), 0.7-0.5 (br, 12H CH_3 alkyl chain PCPDTBT and 6H CH_3 *i*-propyl TIPNO). Mn=14.9 KDa, Mw/Mn=1.8.

2. Ultrafast transient absorption and CW measurements

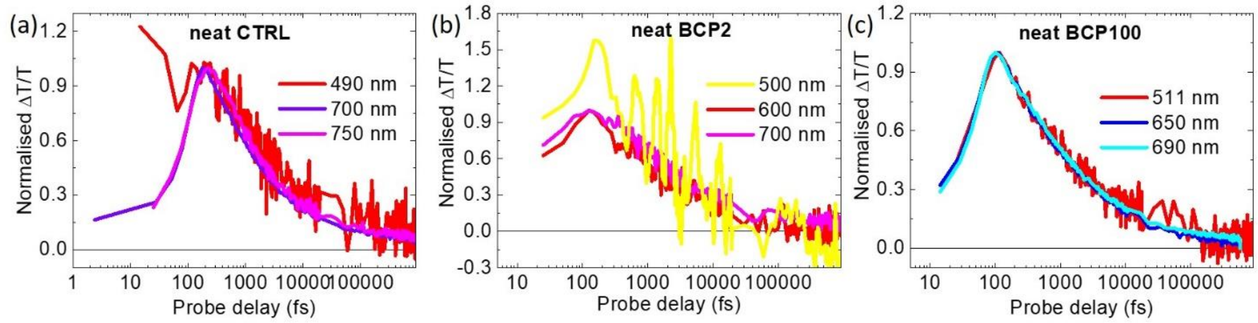


Figure S1 Temporal dynamics of normalised TA signal at different probe wavelengths in neat CTRL films (a), neat BCP2 (b) and BCP100 (c) NP films. Pump excitation: 400 nm.

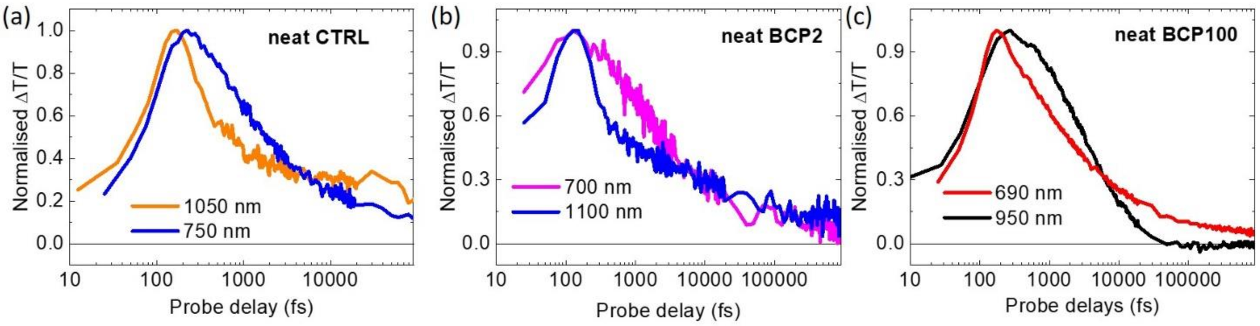


Figure S2 Temporal dynamics of normalised TA signal at different probe wavelengths in the visible and IR spectral region: (a) neat CTRL films, (b) neat BCP2 and (c) neat BCP100 films. Pump excitation: 400 nm**.**

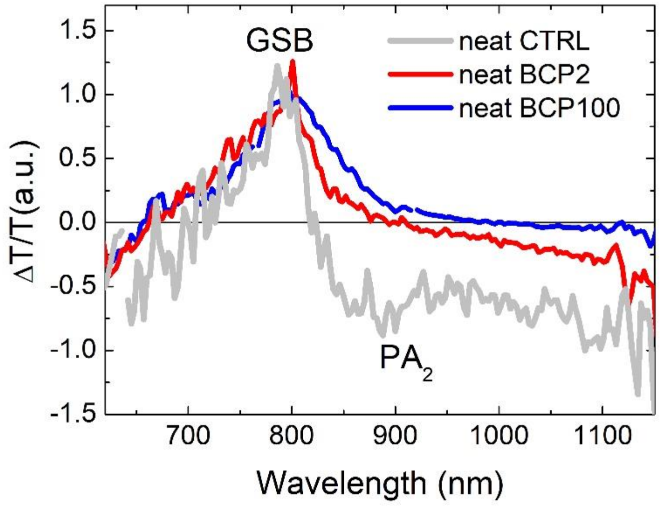


Figure S3 CW Photo Induced Absorption measurements performed on neat control film, neat BCP2 and BCP100 films. In-phase signals ΔT have been obtained by subtracting the background and by normalizing to the sample transmission T. Normalized signals are shown for better comparison.

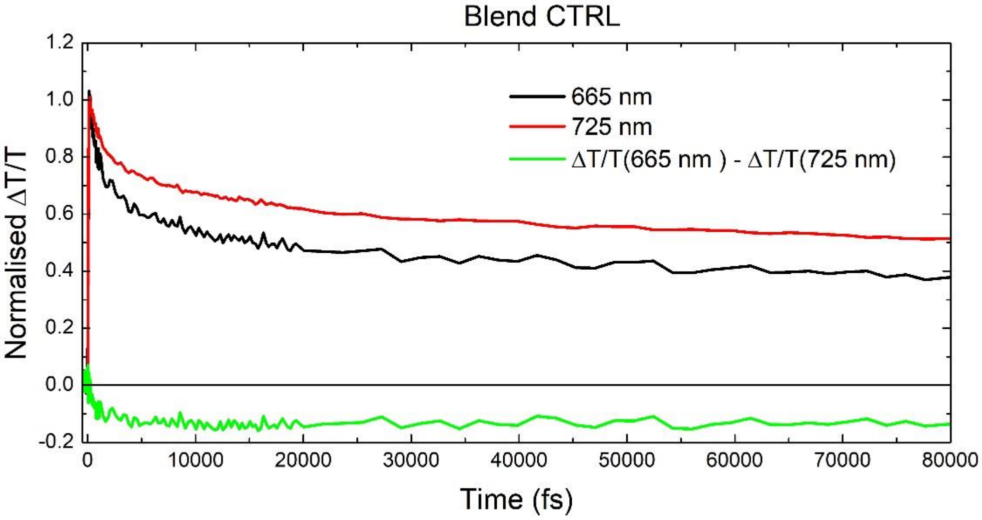


Figure S4 Temporal dynamics of normalised TA signal at 665 nm (black line) and 725 nm (red line) in blend CTRL film. The green line represents the differences between 665 and 725 nm TA signals. Pump excitation: 650 nm.

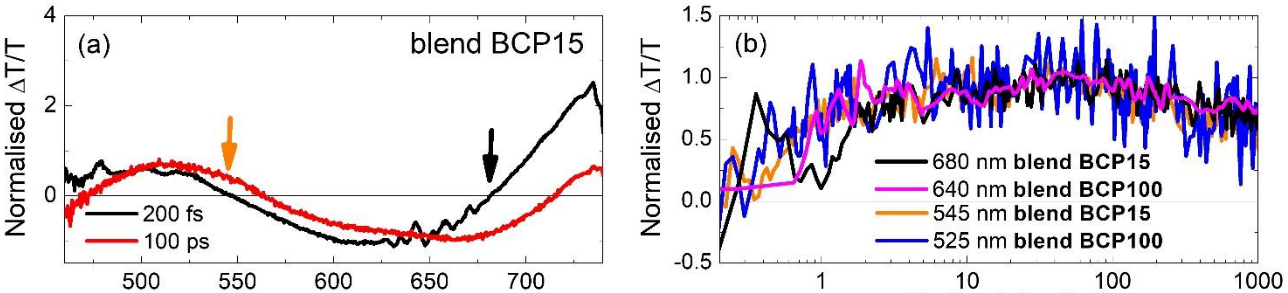


Figure S5 (a) TA spectra in blend BCP15 NPs; spectra at early and long pump-probe delays have been normalized at the minimum of the negative band around 600 nm. (b) Orange and black lines: temporal dynamics at two probe wavelengths (highlighted by arrows in TA spectra) in blend BCP15 NPs. For a comparison temporal dynamics in blend BCP100 NPs are reported (magenta and blue lines). Pump excitation: 650 nm.

References

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