

Supplementary Materials for

Rod-coil block copolymer:fullerene blend water-processable nanoparticles: how molecular structure addresses morphology and efficiency in NP-OPVs

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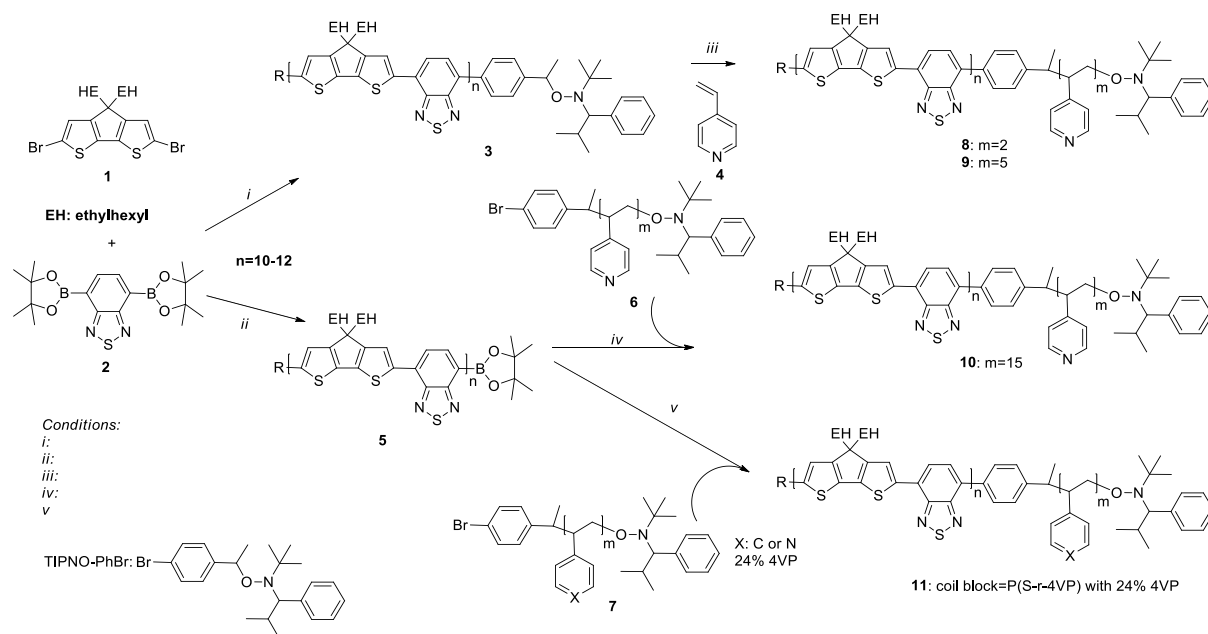
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The four amphiphilic block copolymers studied in this work were synthesized by the procedure depicted in **Scheme S1**, and reported elsewhere. [1-4]



Scheme S1. Synthetic routes for the BCPs used in this work (8 BCP2, 9 BCP5, 10 BCP15, and 11 BCP100, respectively).

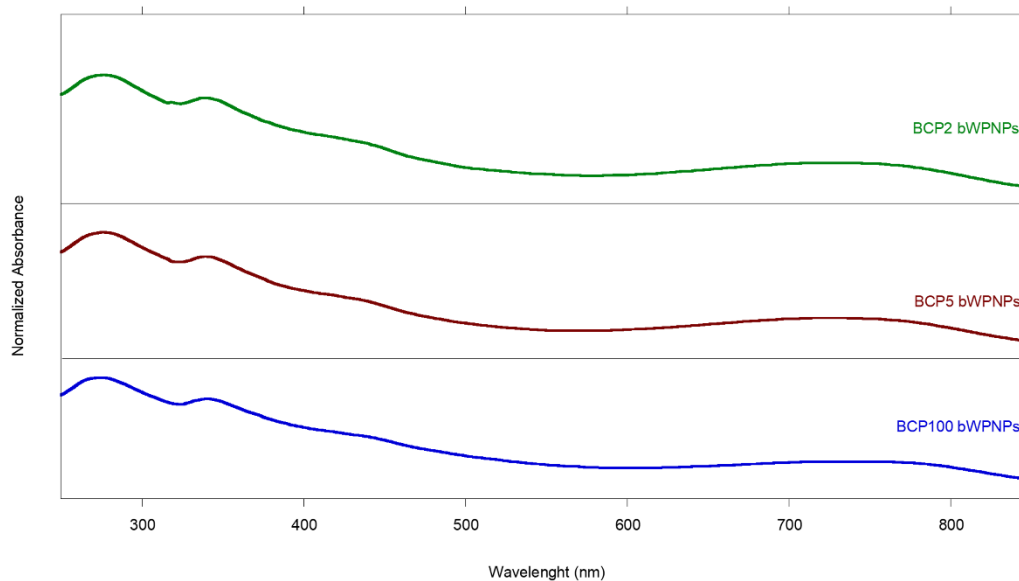


Figure S1. Normalized absorption spectra of BCP2 (green), BCP 5 (red) and BCP100 (blue) bWPnPs dispersion after dilution with water 1:100.

- GIWAXS MEASUREMENTS ON PCBM:BCP=3:1 blend WPNP FILMS

The samples on cleaned glass (1x1 cm²) were prepared in different ways and properly thermally treated before measurements. Details on measurements are elsewhere reported. The list of samples as well as the main structural features are below specified in **Table S1**.

Table S1. Features of BCP blend WPNP films differently treated

sample ^a	D1 ^b	L1	D2 ^c	L2	D3 ^d	L3
BCP15 bWPNNPs	0.86	<3	-	-	0.41	<2
BCP5 bWPNNPs	0.85	3	-	-	0.41	<2
BCP15 bWPNNPs (5 layers)	0.85	3	-	-	0.41	<2
BCP15 bWPNNPs (annealed at 140 °C)	1.05 /0.68 ^e	3	-	-	0.41	<2

^a Both values of d-spacings and L (crystallite dimensions) are expressed in nm.

^b Attributed to macromolecule aggregation

^c Attributed to PCBM

^d Attributed to both glass substrate and disordered copolymer part

^e the second spacing has been observed in a second measurements after six months, possibly due to copolymer degradation.

All the films are largely amorphous, as clearly indicated by both D3 bump and L1 value in **Table S1** and even in case of repeated annealing the majority of the material remains un-crystallized. The observation of multiple aggregation spacings (BCP15 bWPNNP film with 5 layers) is indicative of the materials tendency to poorly ordering, moreover the d-contraction observed in thermally stressed films (BCP15 bWPNNP film annealed at 140 °C) indicate that to reach effective molecular aggregation a simple annealing up to PCBM melt is insufficient.

In **Figure S1** XRD profile of BCP15 bWPNNP film with 5 layers is shown with the indication of the main features, the poor order achieved yields peaks attributed to copolymer weak and broad, while the amorphous part, glass diffraction and PCBM most intense peak occupy the same spectrum area preventing an efficient deconvolution.

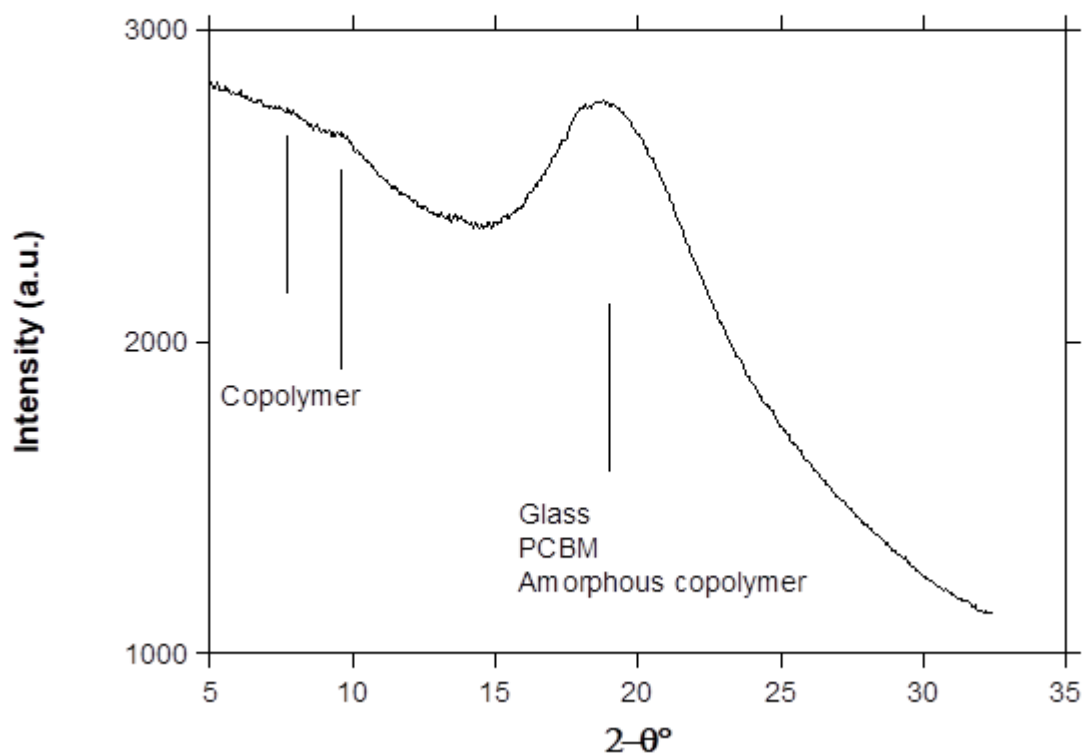


Figure S2. XRD profile extracted from 2D-images of BCP15 bWPNP film with 5 layers, vertical bars indicate diffraction features (see text).

Table S2. Hole mobility calculated through space-charge limited current method of layers deposited from BCP nWPNP suspensions.

WPNP samples (treatment)	hole mobility [cm ² ·V ⁻¹ ·s ⁻¹]
BCP2 nWPNP (as casted)	- ^a
BCP2 nWPNP (annealed 120 °C)	- ^a
BCP5 nWPNP (as casted)	- ^a
BCP5 nWPNP (annealed 120 °C)	4.6 x 10 ⁻³
BCP15 nWPNP (as casted)	1.5 x 10 ⁻⁴
BCP15 nWPNP (annealed 90 °C)	3 x 10 ⁻³
BCP100 nWPNP (annealed 120 °C)	1.3 x 10 ⁻⁴

^aresistive

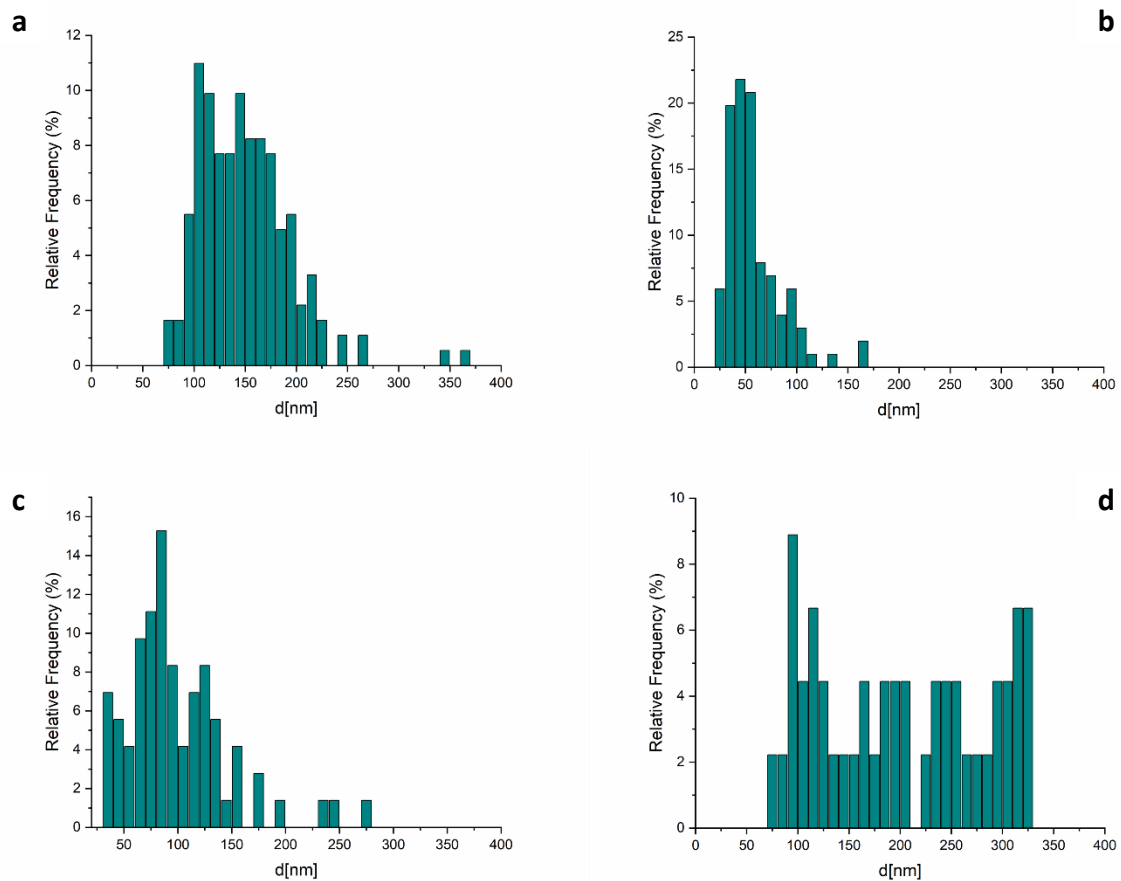


Figure S3. Size distribution of the bWPNNs a) BCP2 bWPNNs b) BCP5 bWPNNs c) BCP15 bWPNNs d) BCP100 bWPNNs.

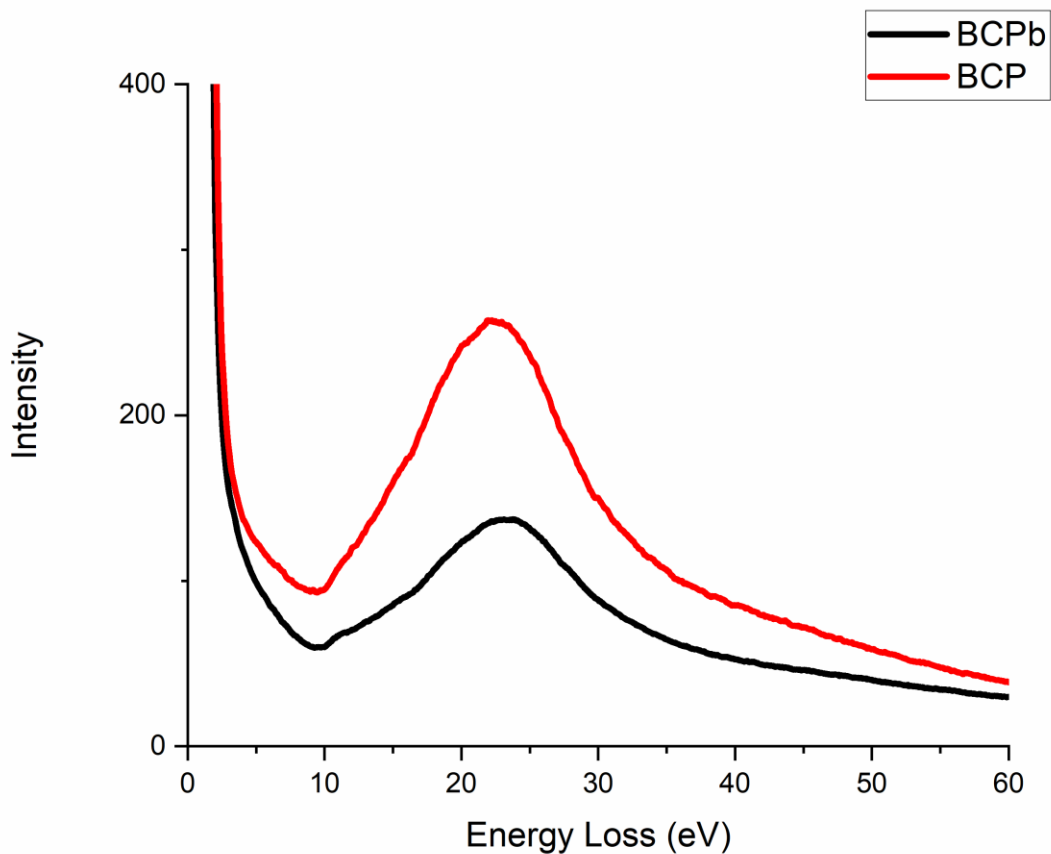


Figure S4. EELS low loss spectra. In red EELS spectra of the nWPNP sample, the plasmon peak is at 22 eV. In black EELS spectra of a BWPNP sample, where the plasmon peak is shifted at 25-26eV because of the superimposition of the nWPNP sample and PCBM plasmon that has the maximum at 30eV [4,5]

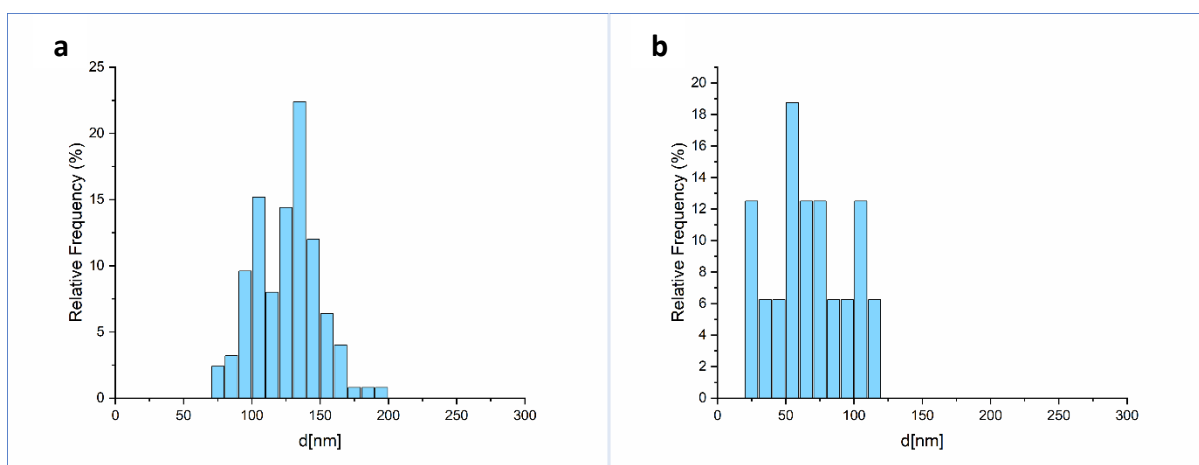


Figure S5. Size distribution of the PCBM rich cores measured for the a) BCP2 bWPNNPs b) BCP15 bWPNNPs.

References

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