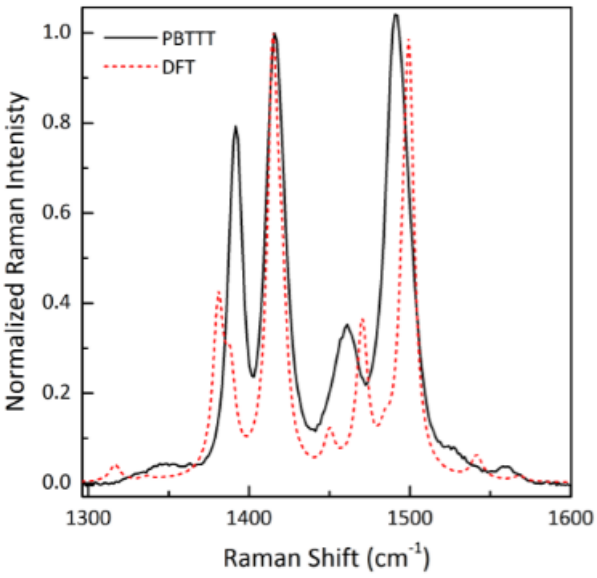
Impact of Fullerene Intercalation on Structural and Thermal Properties of Organic Photovoltaic Blends

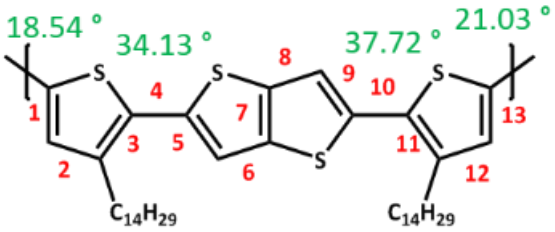
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Raman Mode Assignments

We consider a PBTTT oligomer and calculate at the B3LYP/6-311 G(d,p) level of density functional theory using the Gaussian09 computational suite (Figure SI 1). The C_{14} side chains were replaced with methyl groups to minimize the computational requirement. Neat PBTTT displays four main Raman-active vibrational modes, which we assign to symmetric stretches of the C-C and C=C in T and TT units: C-C_T = 1389 cm^{-1}, C=C_T 1415 cm^{-1}, C-C_{TT} 1467 cm^{-1} and C=C_{TT} 1491 cm^{-1}, respectively (see Figure SI 1). Here, the subscript 'T' refers to the unfused thiophene and 'TT' the fused thienothiophene. The mixed nature of the double bond (C=C) modes arises from four unique environments in one repeat polymer unit; (1) $(C=C)_T$ neighbouring an unfused T, (2) $(C=C)_T$ adjacent to TT, (3) $(C=C)_{TT}$ adjacent to T and (4) inner $(C=C)_{TT}$. The extended spectra show Raman scattering from inter-unit vibrations between 1100 cm^{-1} and 1250 cm^{-1} and C-S bonds between 600 cm^{-1} and 750 cm^{-1}.





Bond Lengths (Å)							
1	1.376	4	1.446	7	1.390	10	1.446
2	1.420	5	1.379	8	1.414	11	1.384
3	1.384	6	1.414	9	1.379	12	1.420

6-311 G (d,p)

Figure SI 1: Experimental Raman spectrum and DFT simulation of PBTTT using the B3LYP functional and 6-311 G(d,p) basis-set. The geometry is optimised for an oligomer of at least three repeat units. The table and figure details the bond-lengths and dihedral angles resulting from the geometry optimisation.

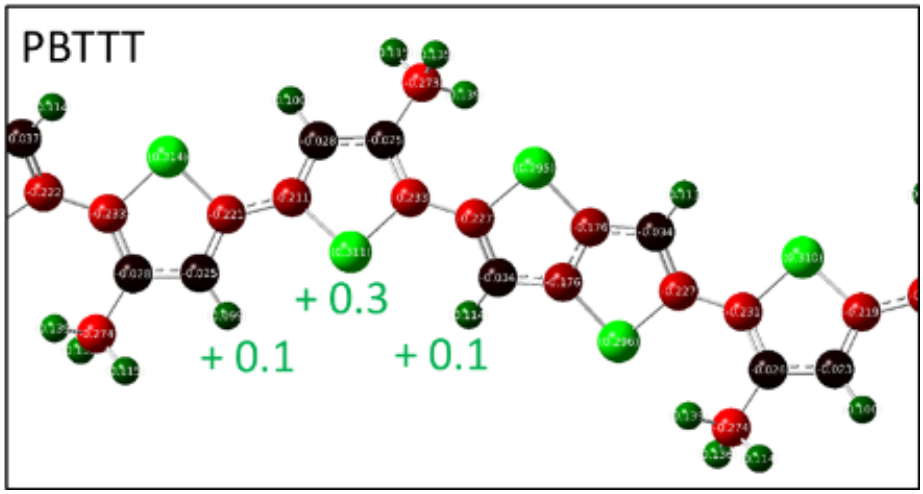


Figure SI 2: Mulliken charges for PBTTT calculated from the optimised structures in Figure SI 1.

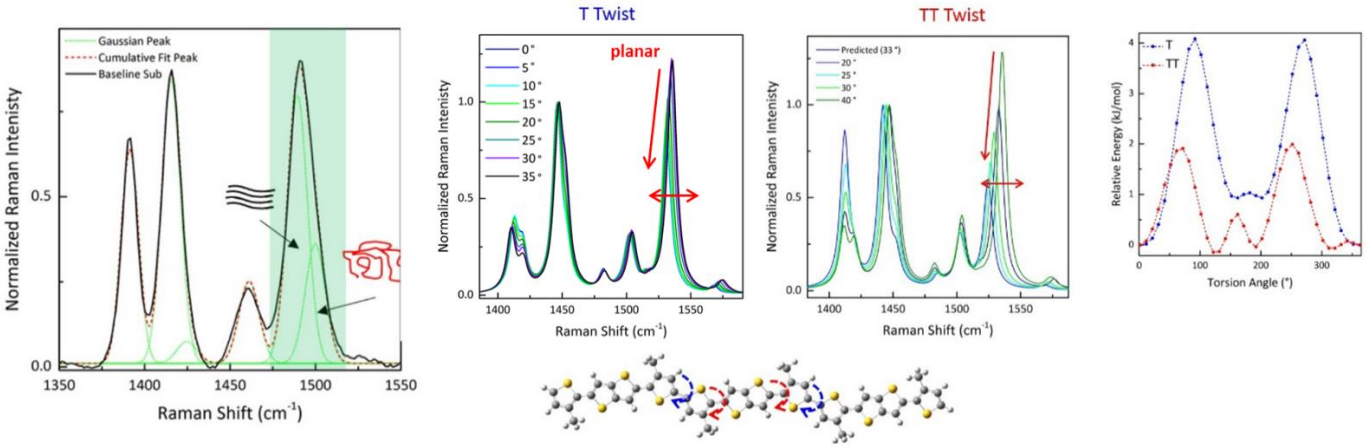


Figure SI 3: (left) Experimental Raman spectra for neat PBTTT and the cumulative fit of a convolution of planar and twisted polymer chains. (right) the simulated Raman spectra arising from a oligomer of PBTTT with frozen dihedral angles (measured in degrees) between the unfused and fused thiophene units.

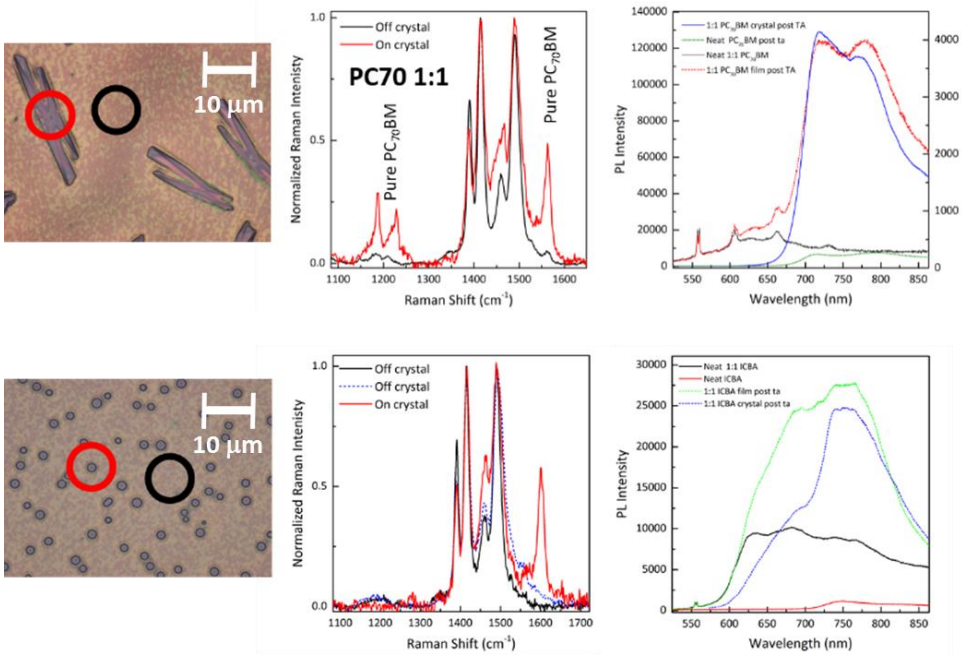


Figure SI 4: (left) optical microscope images of the annealed 1:1 blends with PC70BM (upper) and ICBA (lower). (middle) the corresponding Raman spectra off (black) and on (red) the crystal structures (positions indicated with circles on microscope images). (right) The raw PL spectra of neat films of the blends (black) and acceptors (red), along with PL of the annealed samples off (green) and on (blue) the crystals. The black and green, curves represent the same areas, pre- and post-annealing.

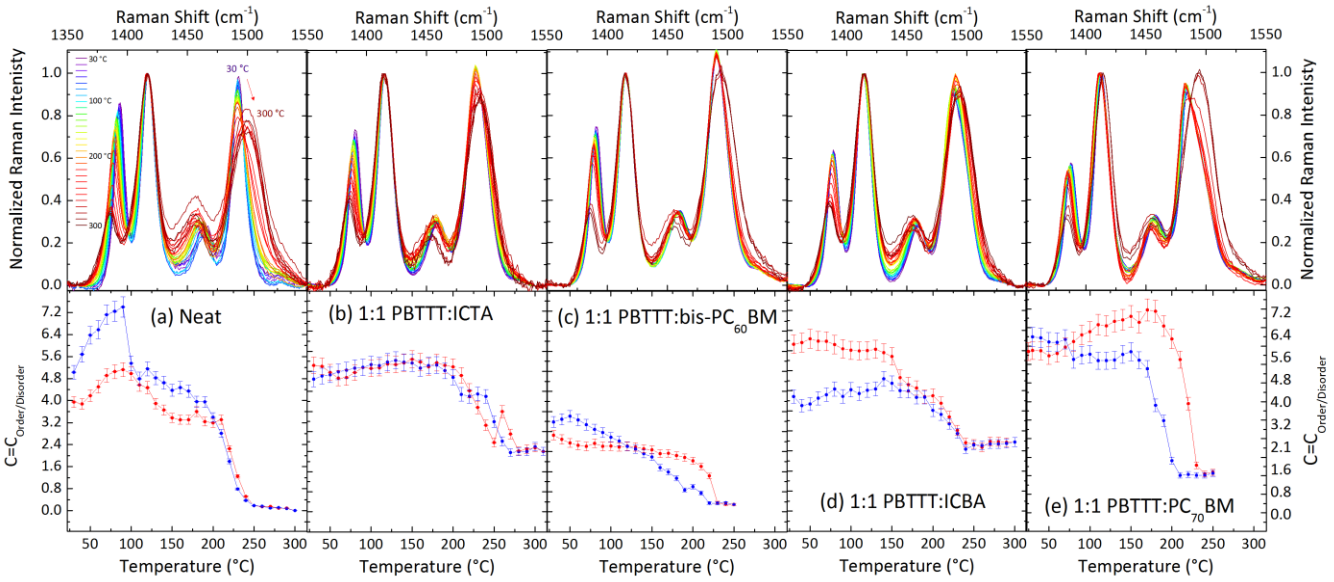


Figure SI 5: (upper) in situ Resonant Raman spectra acquired on heating at 10 °C/minute for the four fullerenes discussed in the text, normalised to $C=C_T$. (lower) Relative intensity of $C=C_{order/disorder}$, corresponding to the proportion of planar/twisted polymer chains for (a) Neat PBTTT, 1:1 blends of PBTTT with (b) ICTA, (c) bis-$PC_{60}BM$, (d) ICBA, (e) $PC_{70}BM$ during heating (red) and cooling (blue).

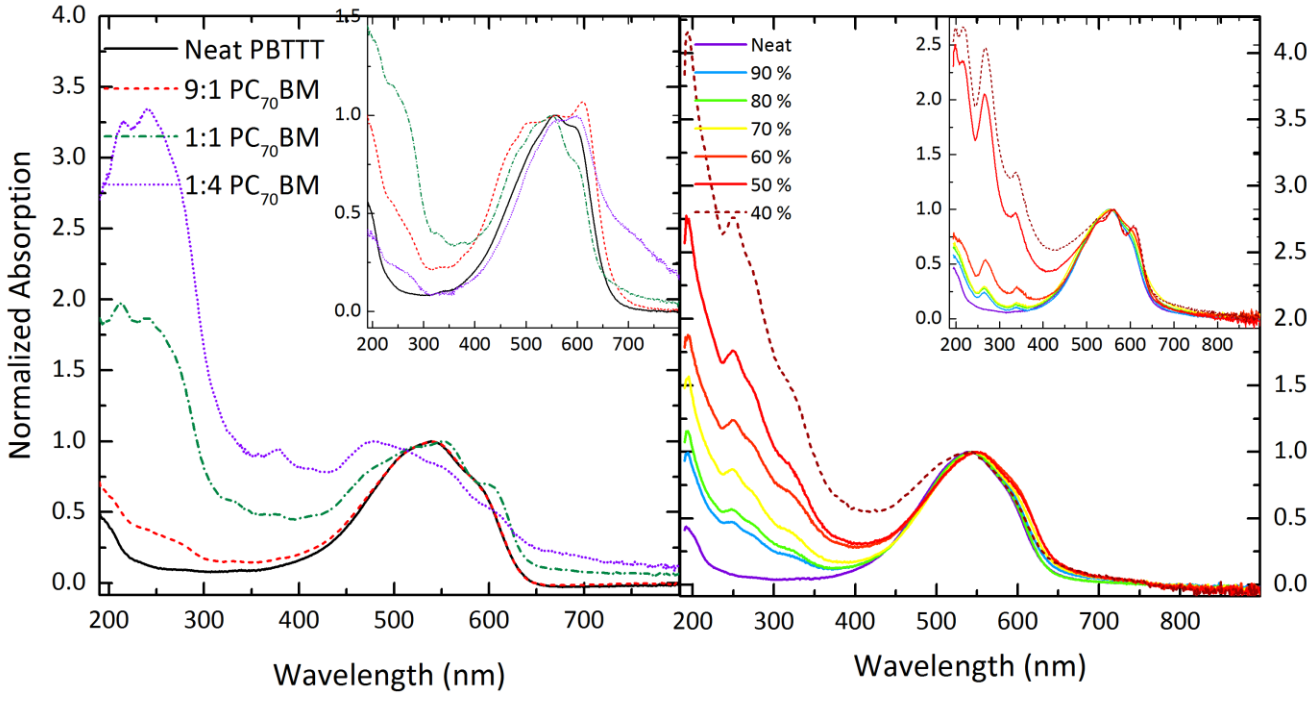


Figure SI 6: Absorption spectra for pristine and annealed (inset) films of PBTTT blended with (left) $PC_{70}BM$ and (right) ICBA, normalized to the main polymer absorption band.

	Roughness (R_q, nm)	
$PC_{70}BM$	Pristine	TA
Neat	2.46	4.78
9:1	2.18	1.80

1:1	0.93	2.00
1:4	0.50	0.75

Table SI 1: Surface roughness (r_q) for PBTTT : $PC_{70}BM$ blends pre and post-annealing extracted from topographical images of the film surface.

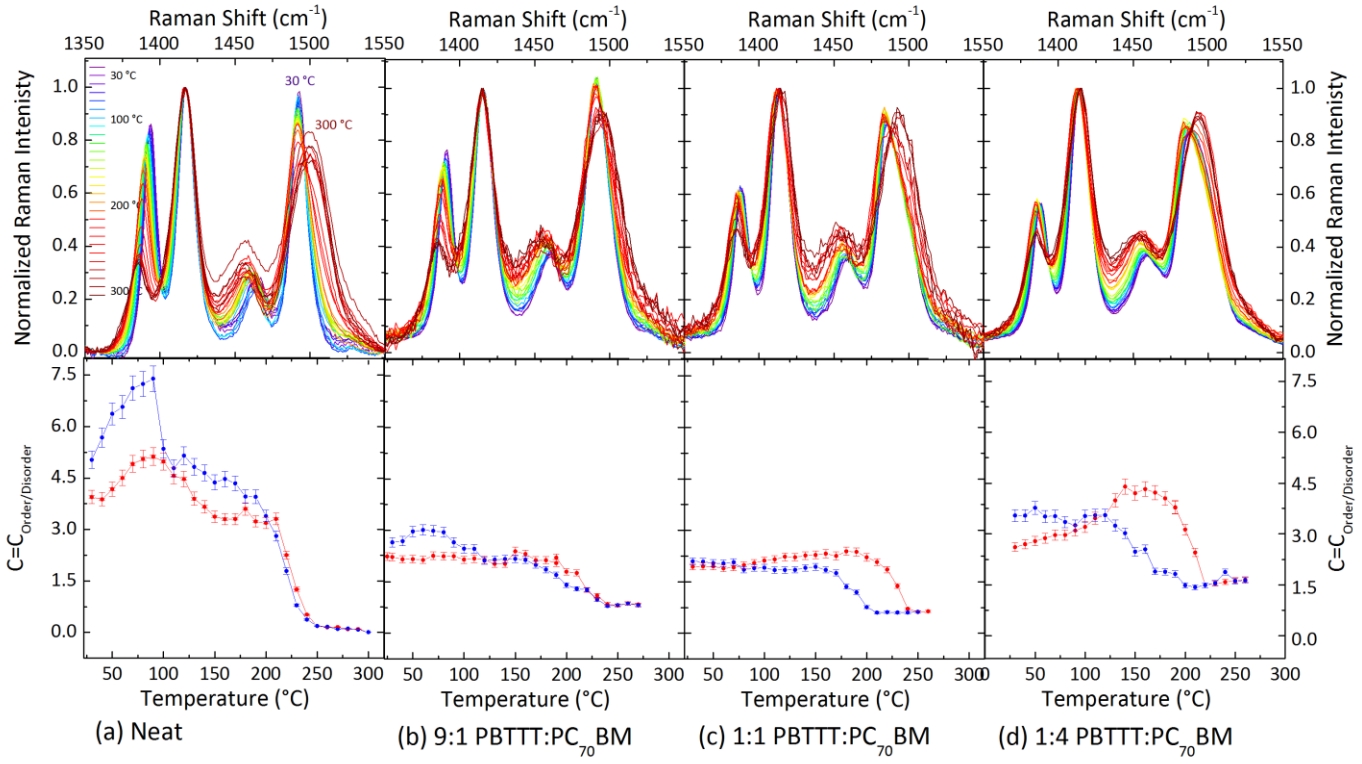


Figure SI 7: (upper) in situ Resonant Raman spectra acquired on heating at 10 °C/minute for four $PC_{70}BM$ loading ratios (0, 9:1, 1:1, 1:4 by weight) discussed in the text. (lower) Relative intensity of $C=C_{order/disorder}$, corresponding to the proportion of planar/twisted polymer chains for (a) Neat PBTTT, 1:1 blends of PBTTT with (b) ICTA, (c) bis-$PC_{60}BM$, (d) ICBA, (e) $PC_{70}BM$ during heating (red) and cooling (blue).