Supplementary Information for

Neutron Radiation Tolerance of Two Benchmark Thiophene-Based Conjugated Polymers: the Importance of Crystallinity for Organic Avionics

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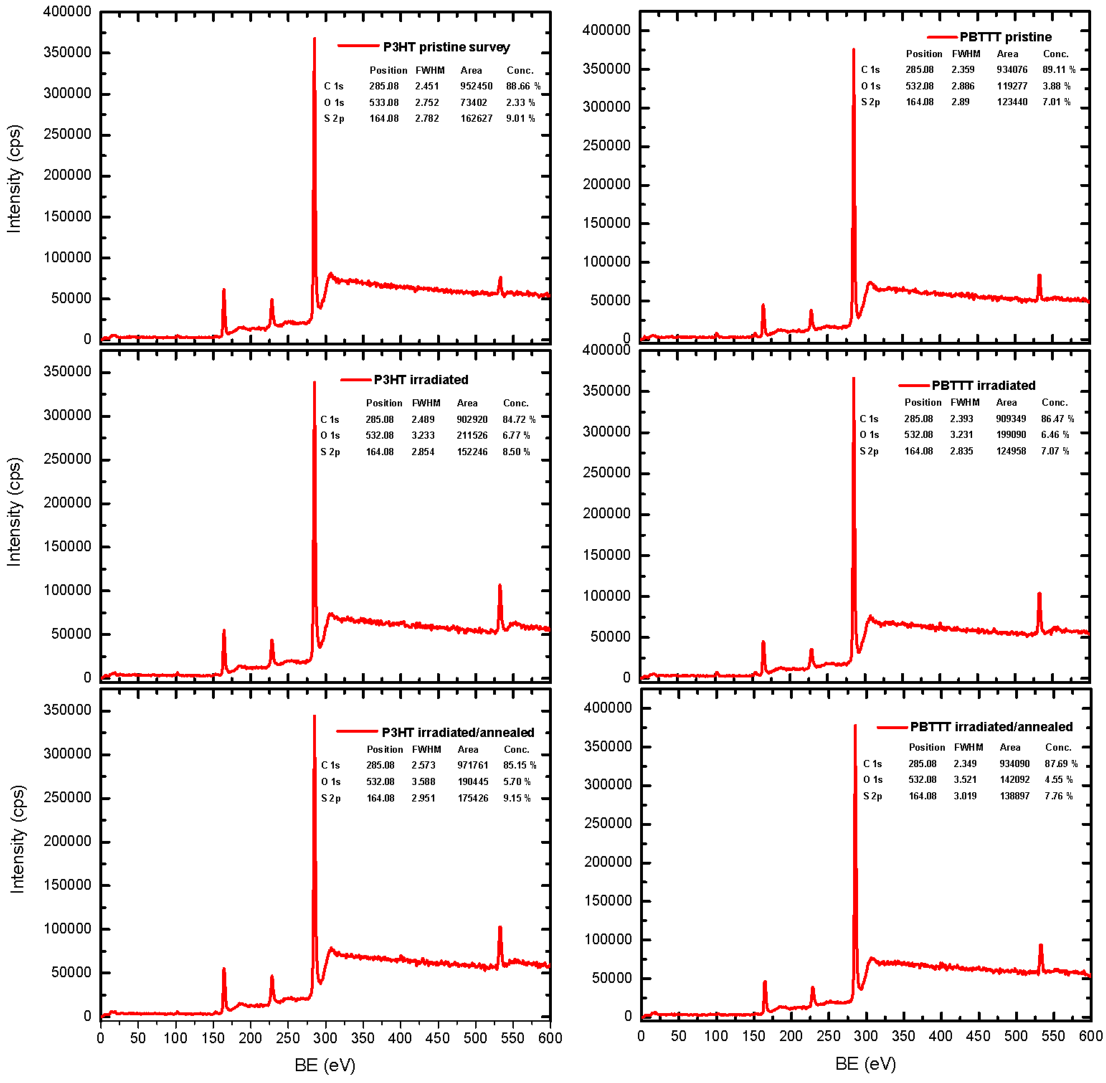
Supplementary Figure S1

The mass concentrations for C (1s), O (1s) and S (2p) were calculated from the peak areas using Casa XPS software. The relative sensitivity factors (R.S.F.) used for C (1s), O (1s) and S (2p) were 1, 2.93 and 1.68, respectively. We can note a small increase of the oxygen content in both irradiated P3HT and PBTTT. However, such an increase is partially reverted by the further thermal annealing.



Supplementary Figure S1: Survey spectra for P3HT and PBTTT pristine, irradiated and irradiated/annealed.

Supplementary Table ST1: XPS fitting results for pristine, irradiated and irradiated/annealed P3HT.

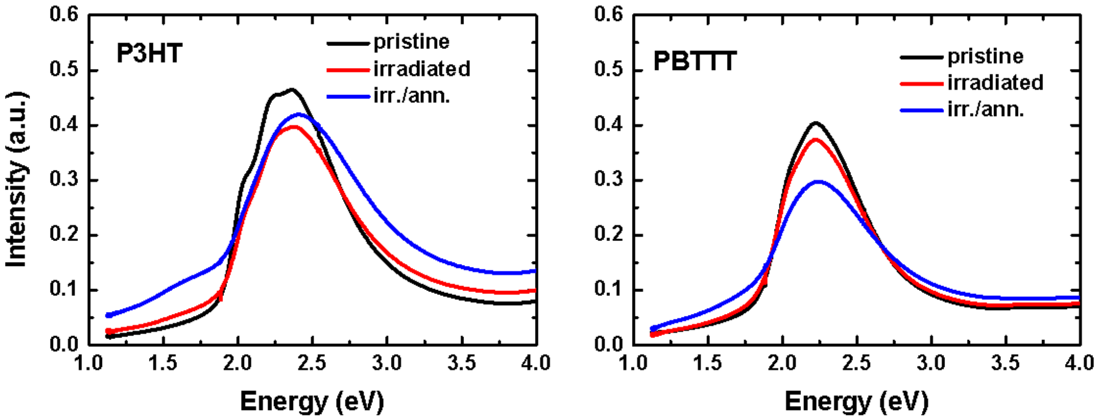
P3HT	Pristine Peak position Mass conc.	Irradiated Peak position Mass conc.	Irradiated/Annealed Peak position Mass conc.
S (2p 3/2) neutral	**163.34 eV 60.88 %**	**163.44 eV 42.14 %**	**163.52 eV 39.65 %**
S (2p 1/2) neutral	**164.54 eV 30.44 %**	**164.64 eV 21.07 %**	**164.72 eV 19.82 %**
Extra component 1	**166.16 eV 8.68 %**	**166.67 eV 14.34 %**	**166.06 eV 17.46 %**
Extra component 2	- - -	**164.02 eV 22.35 %**	**164.06 eV 23.07 %**

Supplementary Table ST2: XPS fitting results for pristine, irradiated and irradiated/annealed PBTTT.

PBTTT	Pristine Peak position Mass conc.	Irradiated Peak position Mass conc.	Irradiated/Annealed Peak position Mass conc.
S (2p 3/2) neutral	**163.60 eV 60.42 %**	**163.70 eV 50.12 %**	**163.70 eV 45.78 %**
S (2p 1/2) neutral	**164.80 eV 30.21 %**	**164.90 eV 25.06 %**	**164.90 eV 22.89 %**
Extra component 1	**166.61 eV 9.37 %**	**167.50 eV 8.42 %**	**167.59 eV 6.17 %**
Extra component 2	- - -	**164.45 eV 16.40 %**	**164.34 eV 25.16 %**

Supplementary Figure S2

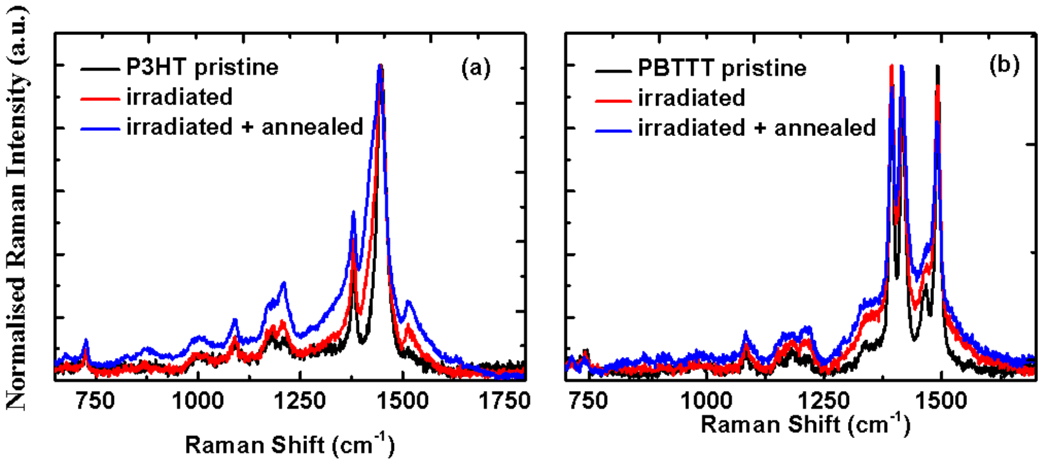
For P3HT, the irradiation leads to a blue-shift, an increase of the sub-gap absorption and a bleaching of the absorption intensity. Interestingly, whereas the first two effects are exacerbated by the post-radiation annealing, we note that such thermal treatment permits a partial recovery of the intensity bleaching. Conversely, for PBTTT the post-irradiation annealing leads to a further bleaching of the intensity, although both the blue-shift and the sub-gap absorption are less evident than in P3HT.



Supplementary Figure S2 UV-Vis absorption spectra for P3HT and PBTTT pristine, irradiated and irradiated/annealed.

Supplementary Figure S3

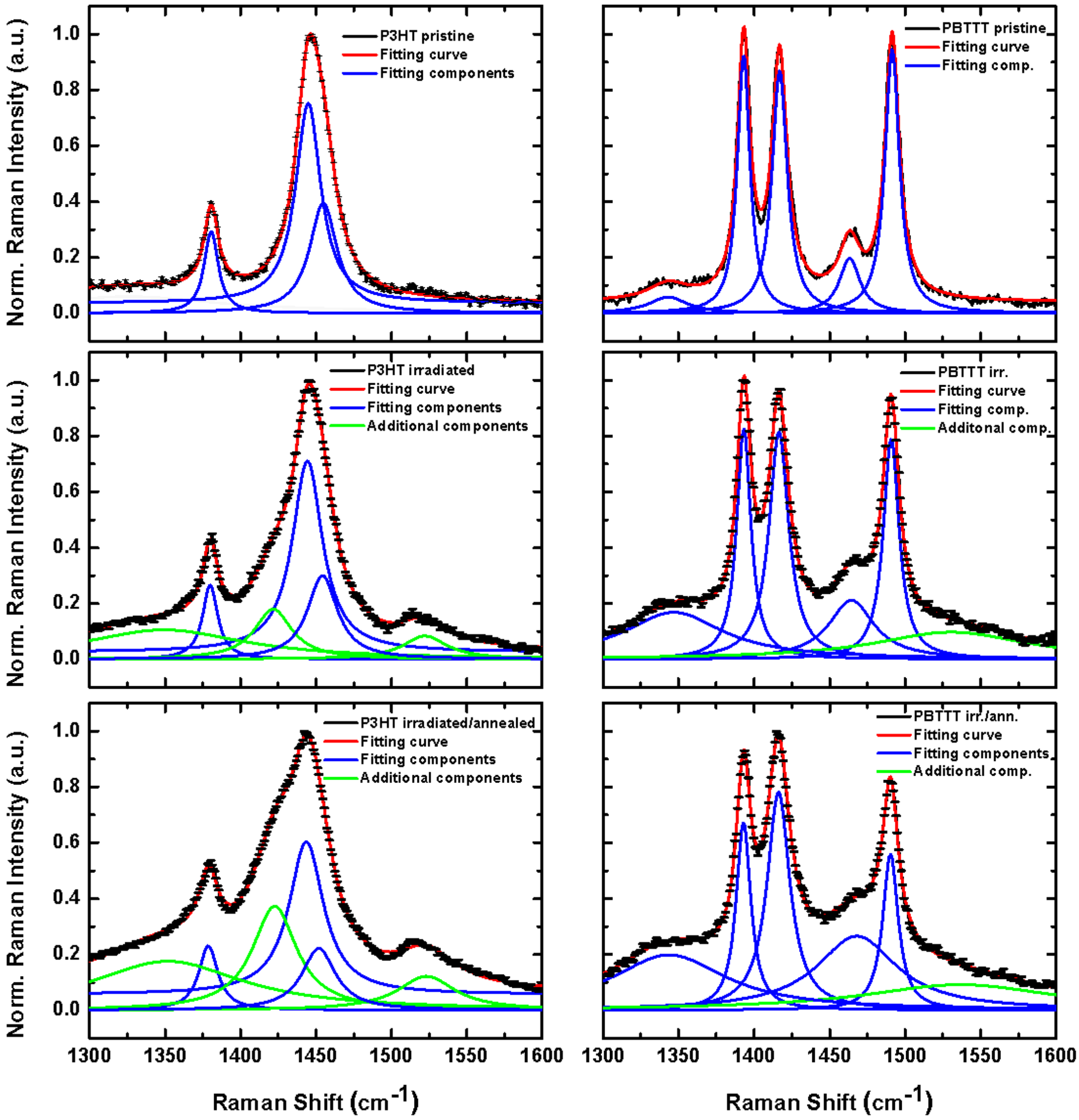
It is worth noting that irradiation and, to a larger extent, the post-irradiation annealing step lead to an increase in the intensity of the C-C inter-ring peak at 1210 cm^{-1}, the C-H bending coupled with the C-C inter-ring mode at 1180 cm^{-1}, the pure C-H bending mode at 1000 cm^{-1}, the C-C_{alkyl} stretching at 876 cm^{-1} and the C-S-C ring deformation peak at 728 cm^{-1}. All those effects seem to be less pronounced for PBTTT.



Supplementary Figure S3: Full Raman spectrum for P3HT (a) and PBTTT (b).

Supplementary Figure S4

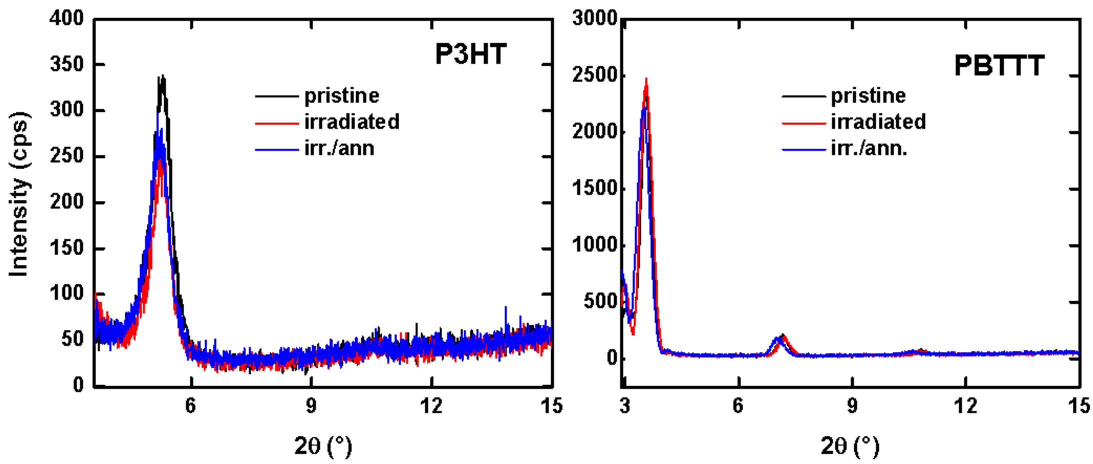
For P3HT, the spectrum of pristine P3HT can be fitted using three Lorentzians, centred at 1380 cm^{-1}, 1445 cm^{-1} and 1455 cm^{-1}. After irradiation, we can observe the development of additional fitting components at 1350 cm^{-1}, 1420 cm^{-1} and 1520 cm^{-1} that keep growing upon further annealing. The last two modes have been ascribed to the C=C stretching mode in the quinoid form and C=C asymmetric stretching, and have been related to the presence of polaronic-like species in chemically doped poly (thiophenes) [ref. 39-41]. For PBTTT, we fitted the 1300-1600 cm^{-1} region with five Lorentzians centred at 1340, 1393, 1418, 1463, and 1493 cm^{-1}. Upon irradiation and post-annealing, we note a strong broadening of the C-C intra-ring mode (1420 cm^{-1}) and the development of an additional fitting component at 1550 cm^{-1}. This can be explained in terms of decreased conformational order after irradiation. In addition, one can note an intensity redistribution between the inter-ring C=C (1418 cm^{-1}) and the intra-ring C=C (1493 cm^{-1}) modes, with an increase of the latter after irradiation and annealing.



Supplementary Figure S4: Fitting of the main in-plane ring modes of P3HT and PBTTT Raman spectra.

Supplementary Figure S5

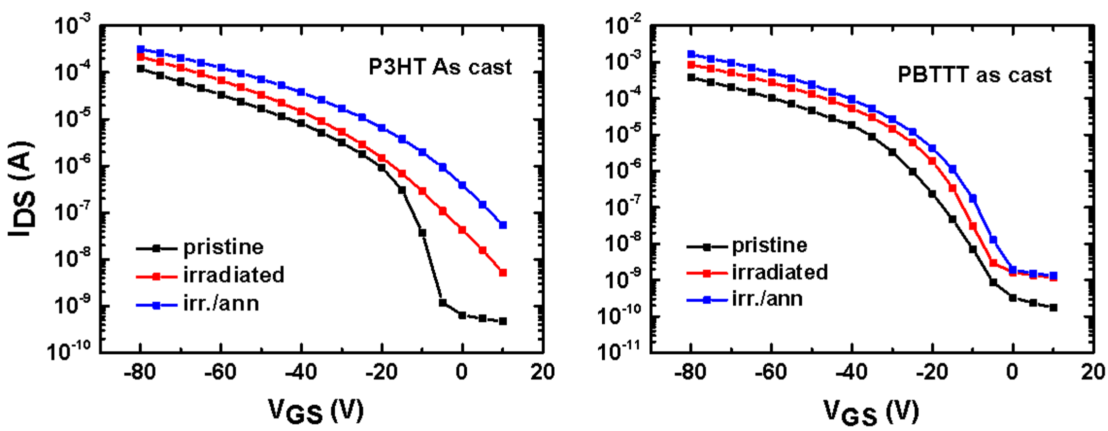
The XRD patterns for both P3HT and PBTTT films show no appreciable differences upon annealing and post-irradiation annealing. It is also worth noting the sharper and more intense <100> peak (lamellar stacking) observed in PBTTT, which indicates a higher crystallinity for this polymer.



Supplementary Figure S5: XRD pattern for P3HT (left) and PBTTT (right) for pristine, irradiated and irr./ann. films.

Supplementary Figure S6 and Supplementary Table ST3

The OFETs characteristics for as-cast films indicate a lower radiation tolerance if the films are not thermally annealed before neutron exposure. This suggests that the crystalline phase may have a prominent role in slowing down the neutron-induced damage. In addition the hole-mobility already increases after irradiation for both the polymers, suggesting that given the lower fraction of trapped radicals in the crystalline phase, the post-irradiation annealing is not necessary in as-cast films to access a high-doping regime.



Supplementary Figure S6: OFETs characteristics for P3HT (left) and PBTTT (right) films that were not thermally annealed before the irradiation process.

Supplementary Table ST3: Hole-mobility values for P3HT and PBTTT films that were not thermally annealed before the irradiation process.

	Mobility pristine ($cm^2\ V^{-1}\ s^{-1}$)	Mobility irradiated ($cm^2\ V^{-1}\ s^{-1}$)	Mobility irradiated & annealed ($cm^2\ V^{-1}\ s^{-1}$)
P3HT as-cast	**0.0046(2)**	**0.0066(3)**	**0.0072(3)**
PBTTT as-cast	**0.015(6)**	**0.020(9)**	**0.025(8)**