

Supporting Information

New Insights into the Molecular Dynamics of P3HT:PCBM Bulk Heterojunction: A Time-of- Flight Quasi-Elastic Neutron Scattering Study

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Scattering cross sections and Quasi-elastic signals

Table S1. Coherent and incoherent scattering cross sections of the samples.

	Scattering cross section (cm ⁻¹)		Incoherent Contribution (%)
	Incoherent	Coherent	
h-P3HT	4.069	0.005	99.88
d-P3HT	0.096	0.445	17.74
h-PCBM	0.743	0.181	80.41
d5-PCBM	0.482	0.225	68.18
h-P3HT: d5-PCBM	2.276	0.115	95.19
h-P3HT: h-PCBM	2.406	0.093	96.28
d-P3HT: d5-PCBM	0.289	0.335	46.31
d-P3HT: h-PCBM	0.420	0.313	57.27

Table S2. Coherent and incoherent relative contributions to the signal.

	P3HT contribution (%)		PCBM contribution (%)	
	Incoherent.	Coherent	Incoherent	Coherent
h-P3HT: d5-PCBM	89.40	2.17	10.60	97.83
h-P3HT: h-PCBM	84.56	2.69	15.44	97.31
d-P3HT: d5-PCBM	16.61	66.42	83.39	33.58
d-P3HT: h-PCBM	11.49	71.09	88.51	28.91

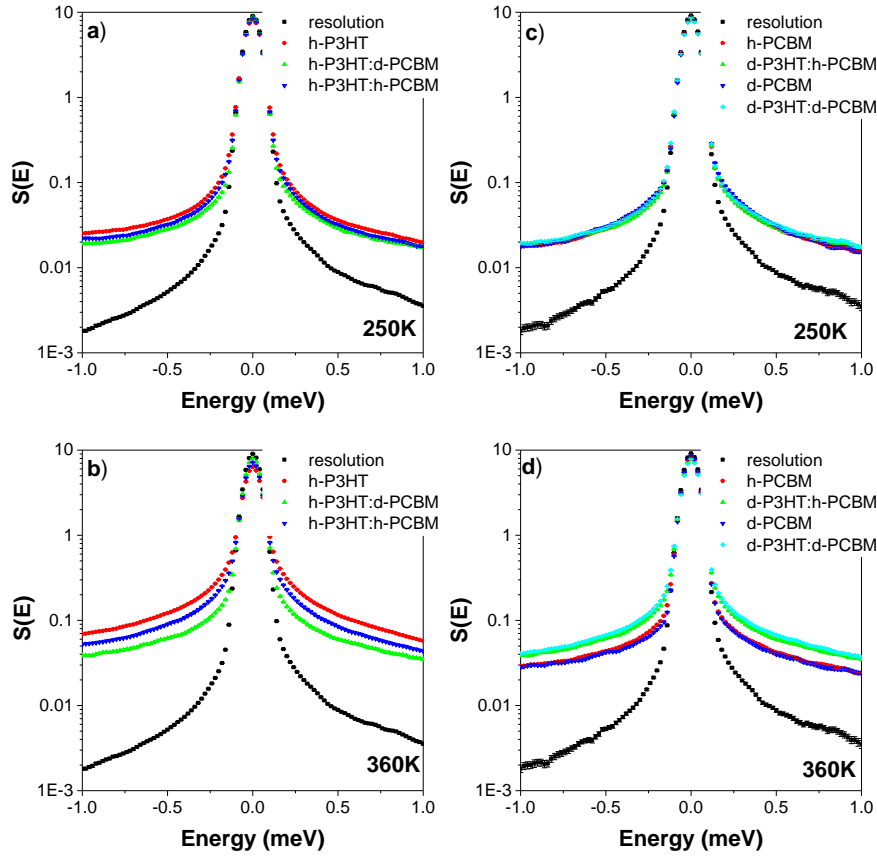


Figure S1. Q-averaged dynamic structure factor for (a and b) h-P3HT, h-P3HT:d-PCBM, h-P3HT:h-PCBM, (c and d) h-PCBM, d-P3HT:h-PCBM, d-PCBM, and d-P3HT:d-PCBM, at 250 K (a and c) and 360 K (b and d). In each case the black dotted spectrum corresponds to data collected at 10 K, to represent the resolution function of the instrument. h-P3HT dynamics is frustrated by both the addition of d-PCBM and h-PCBM but to a lesser extent with the latter one. This is expected due to the larger mass of deuterium. h-PCBM and d-PCBM as well as their blends with d-P3HT behaves similarly.

Intermediate scattering function

The dynamic structure factor $S(E)$ is affected by the instrumental resolution function $R(E)$.

The intermediate scattering function $I(t)$ is calculated by inverse Fourier transforming (IFT)

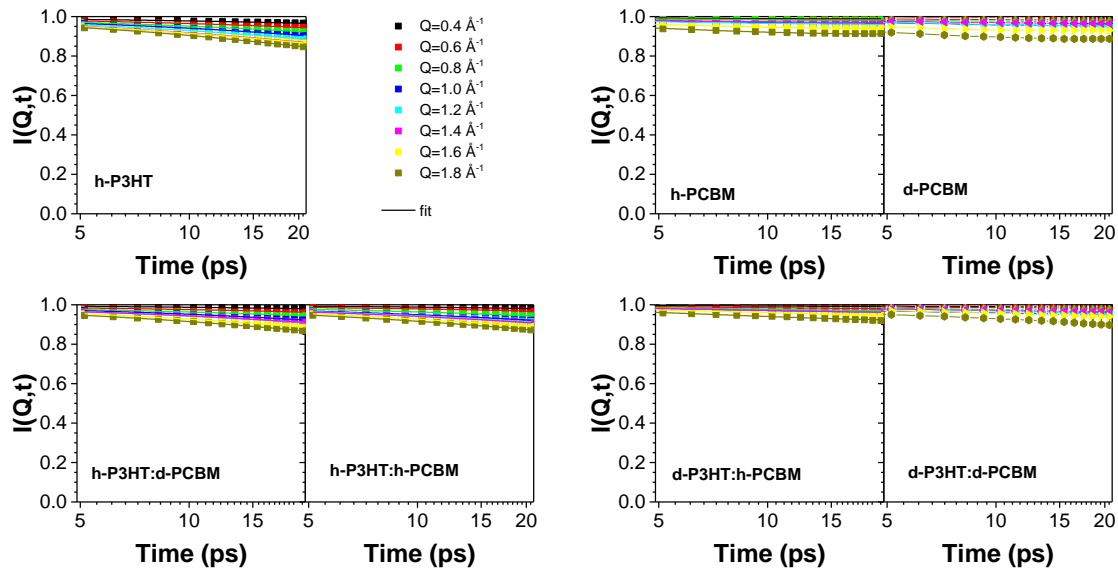
$S(E)$ and $R(E)$:

$$I(t) = \frac{IFT(S(E))}{IFT(R(E))}$$

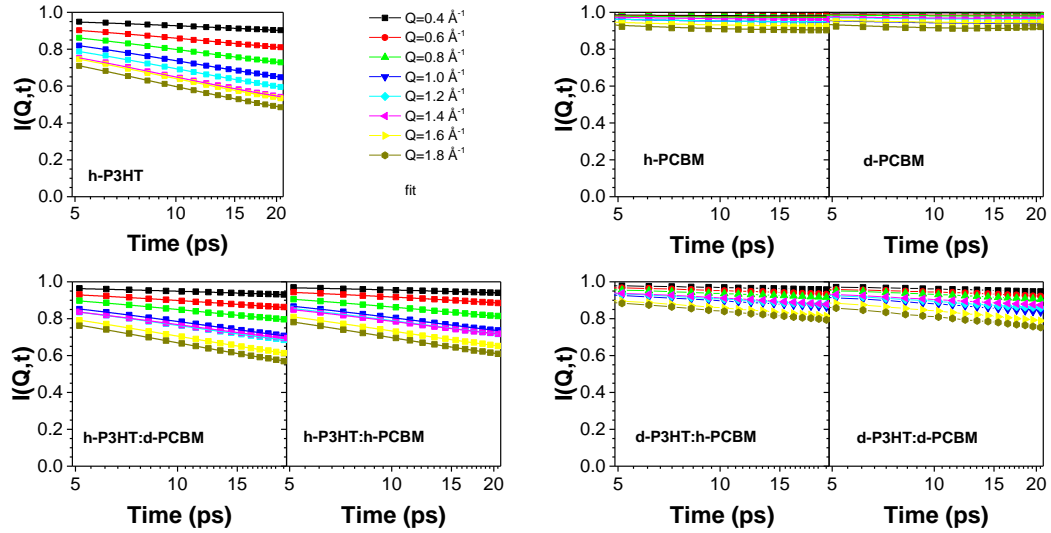
Here the convention for the IFT is:

$$IFT(f(E)) = \frac{1}{h} \int_{-1 \text{ meV}}^{1 \text{ meV}} f(E) e^{i2\pi \frac{E}{h} t} dE$$

where h is the Planck constant. We use the OriginPro 2015 build in inverse fast Fourier transform algorithm. Prior to the IFT, we have smoothed the QENS wing using the adjacent-averaging method with 10 points per windows, remove the background and normalise the spectra so the area of each spectrum is equal to 1.



(a)



(b)

Figure S2. Q-dependence of the intermediate scattering functions (scattered points), at (a) 250 and (b) 360 K, for h-P3HT, h-P3HT:d-PCBM, h-P3HT:h-PCBM, h-PCBM,d-PCBM, d-P3HT:h-PCBM and d-P3HT:d-PCBM. The lines are fits using a stretched exponential model.

Stretched exponential fit

Table S3. Diffusion coefficient and residence time for all the samples at 250 and 360 K.

	D ($\text{\AA}^2 \cdot \text{ps}^{-1}$)		τ_0 (ps)	
	250 K	360 K	250 K	360 K
h-P3HT	0.06 ± 0.02	0.23 ± 0.02	15.9 ± 1.0	8.4 ± 1.0
h-P3HT:h-PCBM	0.03 ± 0.02	0.15 ± 0.02	17.8 ± 1.0	8.3 ± 1.0
h-P3HT:d-PCBM	0.02 ± 0.02	0.12 ± 0.02	20.8 ± 1.0	8.2 ± 1.0
d-P3HT:h-PCBM	0.03 ± 0.02	0.06 ± 0.02	12.7 ± 1.0	11.7 ± 1.0
d-P3HT:d-PCBM	0.04 ± 0.02	0.08 ± 0.02	16.0 ± 1.0	11.6 ± 1.0

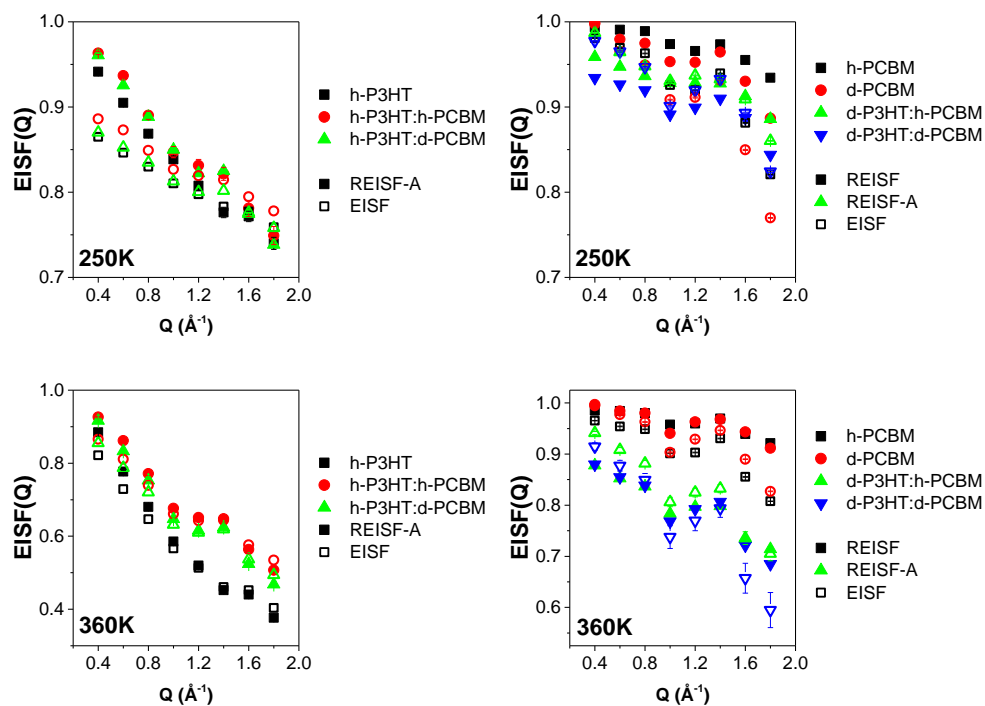
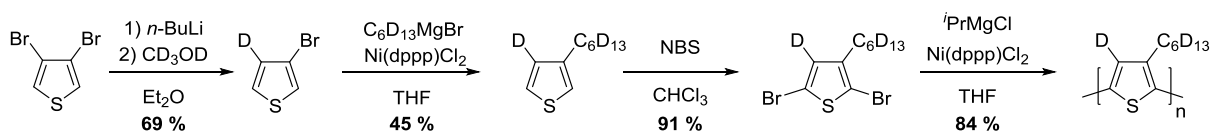


Figure S3. Elastic incoherent factor (EISF) as a function of Q for all the samples at 250K and 360K. The graph shows the impact of the two fitting strategies.

Deuterated P3HT synthesis



4- d_1 -3-Bromothiophene.¹ *n*-Butyllithium (2.5 M in hexanes; 28.0 mL, 70.0 mmol) was added dropwise over a period of 30 minutes to a solution of 3,4-dibromothiophene (7.0 mL, 63.1 mmol) in dry Et₂O (150 mL) at -78 °C. The solution was stirred during 30 minutes at -78 °C, then CD₃OD (5.1 mL, 126.2 mmol) was added dropwise. After a further 5 minutes at -78 °C, the reaction was stirred for 40 minutes at room temperature. The reaction mixture was poured into water, extracted with diethyl ether and washed successively with water and brine. The organic phase was dried over anhydrous MgSO₄, filtered and the solvent was removed under vacuum. The crude was subjected to distillation (80 °C, 20 mbar) to afford the title

compound (7.120 g, 43.4 mmol, 69 %) as a colorless oil. ^1H NMR(400 MHz, CDCl_3): δ (ppm) 7.30 (d, $J = 3.1$ Hz, 1H), 7.26 (d, $J = 3.2$ Hz, 1H).

4- d_1 -3-hexyl- d_{13} -thiophene.² To a stirred magnesium (0.494 g, 20.3 mmol) suspension in dry THF (15 mL) was added dropwise 1-bromohexane- d_{13} (2.3 mL, 16.3 mmol). On complete addition, the mixture was refluxed for 2 hours and was then cooled down at 0°C . A solution of 4- d_1 -3-bromothiophene 2.670 g, 16.3 mmol) with $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.045 g, 0.005 eq) in THF (10 mL) was added to the reaction mixture. The mixture was stirred at 40°C for 24 h and quenched with HCl (aq., 0.1 M). The product was extracted with DCM, washed with water, dried over anhydrous MgSO_4 and concentrated. The crude was subjected to distillation (110°C , 20 mbar) to afford the title compound (1.330 g, 7.3 mmol, 45 %) as a colorless oil. ^1H NMR(400 MHz, CDCl_3): δ (ppm) 7.23 (d, $J = 3.0$ Hz, 1H), 6.91 (d, $J = 2.9$ Hz, 1H).

2,5-dibromo-4- d_1 -3-hexyl- d_{13} -thiophene. NBS (3.542 g, 19.9 mmol) was added to a solution of 4- d_1 -3-hexyl- d_{13} -thiophene (1.650 g, 9.0 mmol) in 30 mL of CHCl_3 . The solution was stirred overnight at room temperature. The product was extracted with DCM, washed with water and dried over anhydrous MgSO_4 . Solvent evaporation and subsequent purification by column chromatography (silica gel, petroleum ether) yielded a colorless liquid (2.786g, mmol, 91 %).

d -P3HT.² To a solution of 2,5-dibromo-4- d_1 -3-hexyl- d_{13} -thiophene (2.070 g, 6.1 mmol) in dry THF (25 mL) was added isopropylmagnesium chloride (1.3 M in THF, 4.7 mL, 6.1 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 h and was then added to a suspension of $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.033 g, 0.01 eq) in 10 mL of dry THF. The polymerisation was stirred at 35°C overnight. The polymerisation was terminated by addition of HCl (aq., 5.0 M, 1 mL) followed again by stirring at room temperature for 5 minutes. The mixture was added dropwise to well stirred methanol (100 mL). Obtained

precipitates were Soxhlet extracted under argon atmosphere in acetone, hexane and chloroform. The chloroform solution of polymer was concentrated and precipitated in methanol. Obtained polymer (0.930 g) was dried under high vacuum for 24 h. Yield = 84 %. GPC (CB): $M_n = 30$ kg/mol, $M_w = 48$ kg/mol, PDI = 1.5.

Material processing

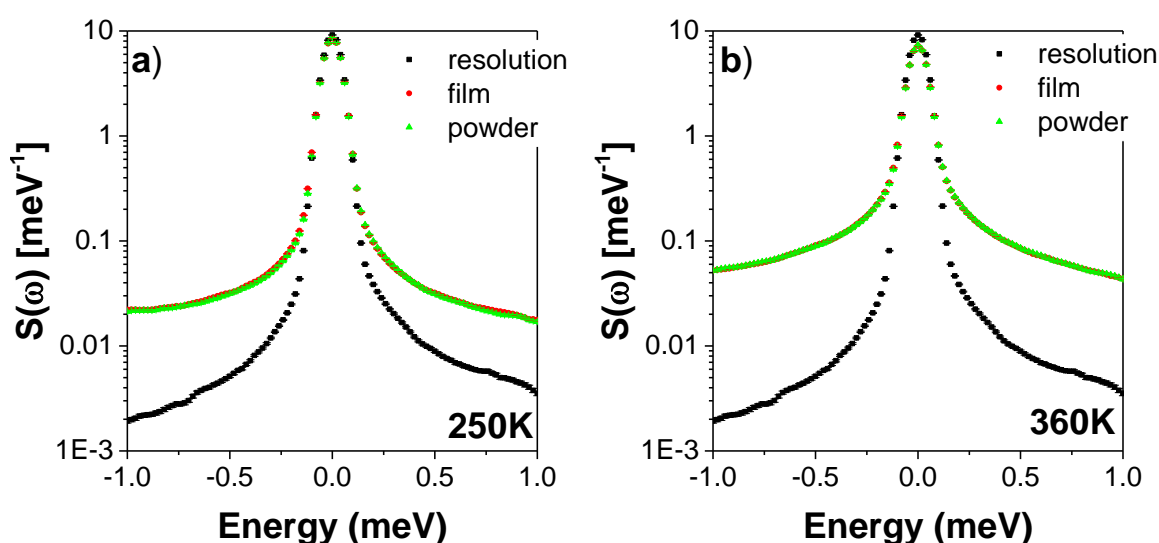


Figure S4. Dynamic structure factor for pressed (film) and non-pressed (powder) samples of h-P3HT:h-PCBM at 250K (a) and 360K (b). The signals have been averaged over the different scattering vector lengths. The black dots (or signal at 10K) represent the resolution function of the instrument. No differences in dynamics can be observed for the two types of samples.

REFERENCES

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(2) Tournebize, A., Bussière, P.-O., Rivaton, A., Gardette, J.-L., Medlej, H., Hiorns, R. C., Norrman, K.. New Insights into the Mechanisms of Photodegradation/Stabilization of P3HT:PCBM Active Layers Using Poly(3-hexyl- d 13 -Thiophene). *Chem. Mater.*, **2013**, *25*, 4522–4528.