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Quantitative insights into the phase behaviour and miscibility of organic photovoltaic active layers from the perspective of neutron spectroscopy

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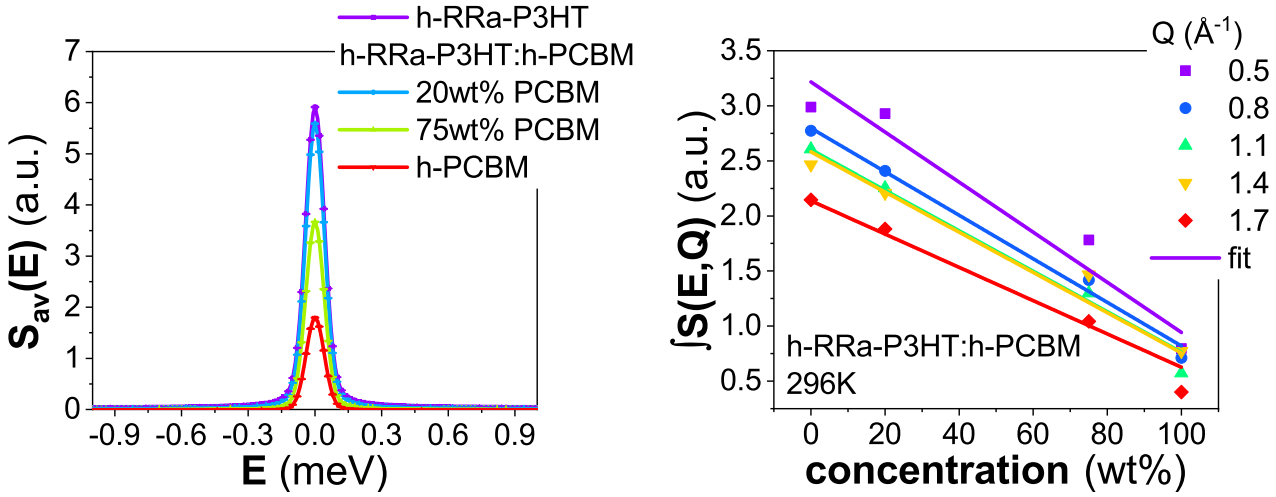
Determination of the macroscopic scattering cross-section



(a) (b)

Figure 1: (a) Mass-normalized QENS spectra of samples h-RRa-P3HT, h-RRa-P3HT:h-PCBM with 20wt% and 75wt% h-PCBM and neat h-PCBM. (b) Integral of the QENS signals between -1 and 1 meV as a function of h-PCBM concentration for different Q values.

The macroscopic neutron cross-section Σ depends not only on the tabulated cross section for each atom composing the material but also on the density of the material. The density changes non-linearly with temperature, especially around the glass transition. The QENS spectra, presented in Figure 1a, are proportional to the structure factors multiply by the Q-independent total (coherent and incoherent) neutron scattering cross section of the samples. Thus, by fitting globally the Q- and concentration-dependent integral of the QENS spectra (Figure 1b) using Equation 1, we can evaluate both the macroscopic neutron cross-sections Σ and the densities of the materials (Table 1).

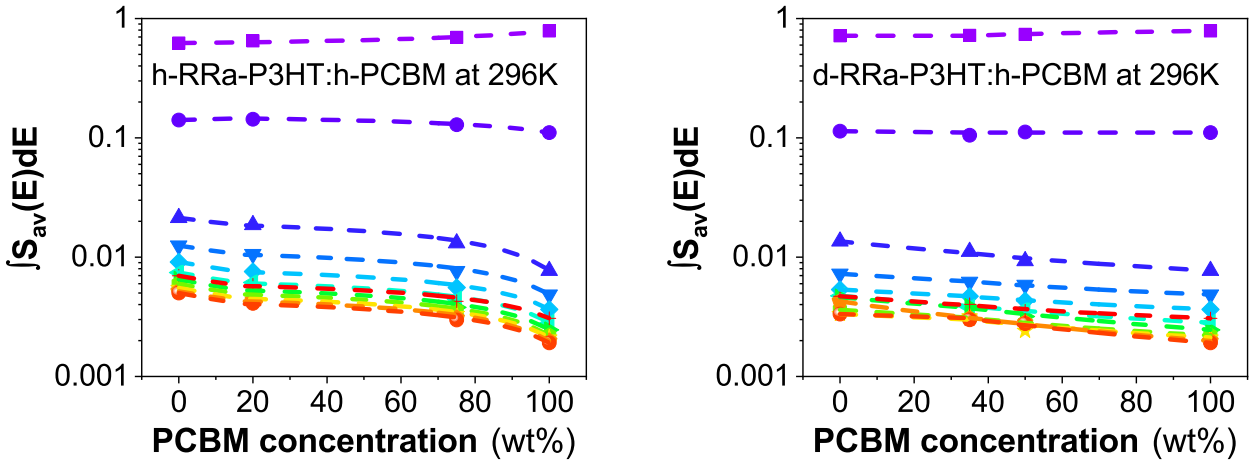
$$\begin{aligned}\int_{-1meV}^{+1meV} S(\mathbf{Q}, E, c_0, T) &\propto \Sigma(c_0, T) \\ &\propto \{(1-c_0) \times d_{P3HT}(T) \times \frac{N_A}{Mw^{P3HT}} \times \sigma_{P3HT} \\ &+ c_0 \times d_{PCBM}(T) \times \frac{N_A}{Mw^{PCBM}} \times \sigma_{PCBM}\}\end{aligned} \tag{1}$$

where c_0 is the PCBM concentration in the sample, N_A is the Avogadro constant, Mw^X is the molecular weight of the monomer for P3HT and the whole molecule for PCBM, d_X is the density and σ_X is the neutron cross section. We choose the symmetric [-1;+1] meV energy window as the spread of the QENS spectra is well enough described within this range. We obtained reasonably accurate density values, as the density of polymers is usually around 1.1 g.cm^{-3}, and PCBM density is reported to be as high as 1.5 g.cm^{-3}. Furthermore, the chosen sample concentrations ensure that the QENS spectra are mainly incoherent and will be considered as such in the following.

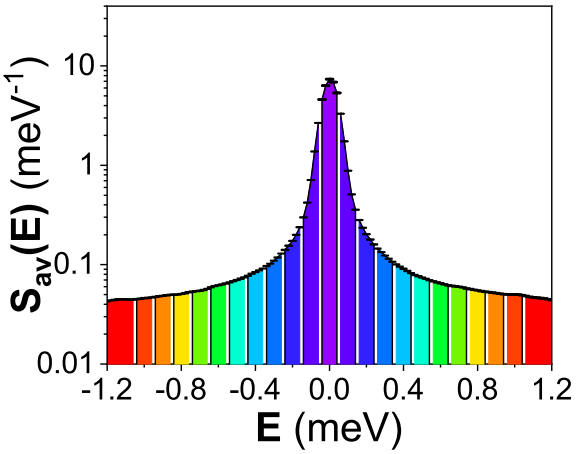
Table 1: Monomer molecular weight (Mw) and neutron cross section (σ) are estimated from tabulated data, while density (d) and macroscopic neutron cross-sections (Σ) are extracted from fits of the QENS spectra using Equation 1.

	h-RRa-P3HT (296K)	d-RRa-P3HT (360K)	h-PCBM (296K)	h-PCBM (360K)
Mw^X (g.mol^{-1})	166.28	179.89	911.00	911.00
σ_X (barn)	1025	171	1556	1556
d_X (g.cm^{-3})	1.111	1.127	1.380	1.538
Σ_X (cm^{-1})	4.826	0.645	1.423	1.585

Evaluating the phase composition of the blends



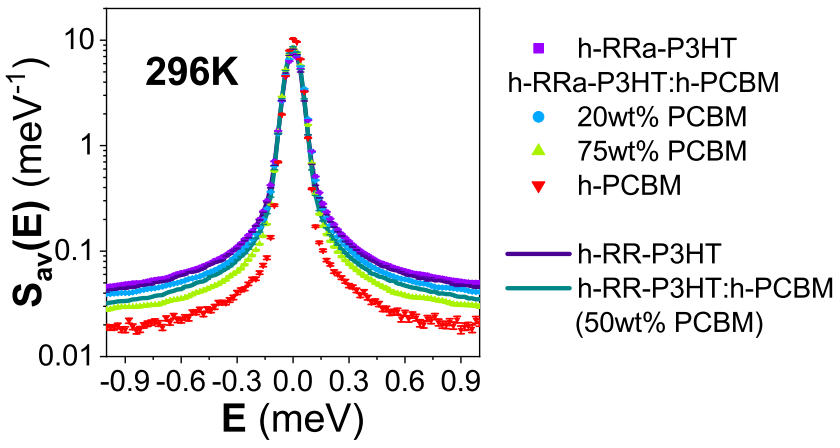
(a) (b)



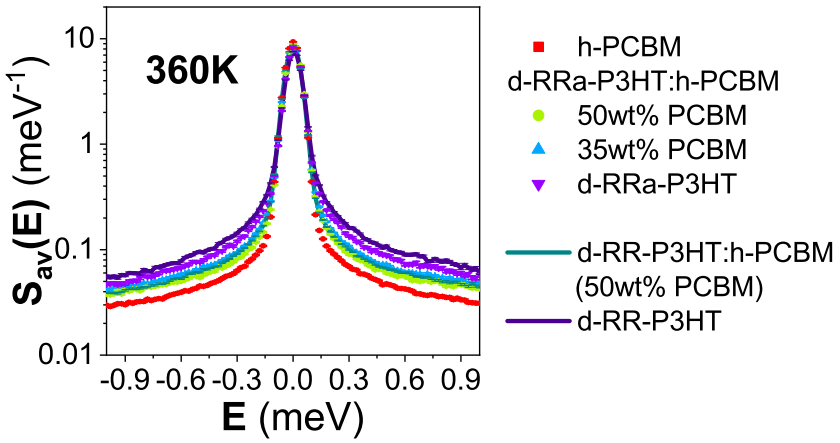
(c)

Figure 2: Concentration-dependent integrals (scatter points) of the Q-averaged QENS spectra on intervals of 0.1 meV as shown in (c) of h-RRa-P3HT:h-PCBM at 296K (a) and d-RRa-P3HT:h-PCBM at 296K (b). The lines are fits using logistic functions-based Equation 3 in the manuscript.

Comparison with blends of regio-regular P3HT and PCBM



(a)



(b)

Figure 3: Q-averaged QENS spectra of (a) neat h-RRa-P3HT, blends of h-RRa-P3HT:h-PCBM of 20 wt% and 75 wt% h-PCBM concentration and neat h-PCBM compared with neat h-RR-P3HT and the blend h-RR-P3HT:h-PCBM of 50wt% h-PCBM at 296K[1] and (b) neat d-RRa-P3HT, blends of d-RRa-P3HT:h-PCBM of 35 wt% and 50 wt% h-PCBM concentration and neath-PCBM compared with the blend d-RR-P3HT:h-PCBM of 50wt% h-PCBM and neat d-RR-P3HT at 360K.[1,2]

References

1 A. A. Y. Guilbert, M. Zbiri, M. V. C. Jenart, C. B. Nielsen and J. Nelson, *The Journal of Physical Chemistry Letters*, 2016, **7**, 2252–2257.

2 A. A. Guilbert, M. Zbiri, P. A. Finn, M. Jenart, P. Fouquet, V. Cristiglio, B. Frick, J. Nelson and C. B. Nielsen, *Chemistry of Materials*, 2019, **31**, 9635–9651.