SUPPORTING INFORMATION

Different Agglomeration Properties of PC$_{61}$BM and PC$_{71}$BM in Photovoltaic Inks – A Spin-Echo SANS Study

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DAB model applied to SESANS

The structural length scale probed (z) is a function of neutron wavelength (λ), magnetic field strength (B) and the inclination angle of the magnets (θ).

$$z = cBL\lambda^2 \cot \theta \qquad (1)$$

where c is a constant, L is the separation between the magnets. Hence using a pulsed source with multiple wavelengths allows us to collect and probe a wide range of length scales simultaneously due to the λ^2 dependence. This also allows us to measure quickly and opens up the possibilities of kinetics studies. In SESANS the measured polarisation is given by;

$$P(z)=P_s/P_0=\exp[\Sigma_t(G(z)-1)] \qquad (2)$$

Where P_s and P_0 are the sample and empty polarisations respectively. The measured correlation function *(G(z))* is a projection of the autocorrelation function $\gamma(r)$ of the density distribution of the sample along the encoding direction of SESANS. Σ_t is the fraction of neutrons that are scattered once and is given by;

$$\Sigma_t = \xi(\Delta\rho)^2 \phi(1-\phi)\lambda^2 t \qquad (3)$$

,where t is the sample thickness, $\Delta\rho$ is the difference in scattering length densities between the two phases as given in Table 1 (Supplementary Information) and ξ is given by;

$$\xi = 2\int_0^\infty \gamma(r)dr \qquad (4)$$

In this case of the DAB model, $\gamma(r)$ is given by;

$$\gamma(r) = \exp(-r/a) \qquad (5)$$

,where a is the average correlation length of a system with random distributed holes and solid and hence $\xi = 2a$ for DAB model. G(z) can be obtained from the Abel transform of the autocorrelation function ($\gamma(r)$), which is given by;

$$G(z) = \left(\frac{z}{a}\right)K_1\left(\frac{z}{a}\right) \qquad (6)$$

, where $K_1[\frac{z}{a}]$ is the first order of the modified Bessel function of the second kind.

Hence in the DAB model there are only two parameters needed to describe the fit: a length scale (a) and the saturation value Σ_t. For a known scattering length density difference, equation (3) can be solved and the roots of this solution yield the two volume fractions of the solvent and aggregate fractions given by;

$$\phi_{agg} = \frac{1 + \sqrt{1 - 4\left(\dfrac{\Sigma_t}{2a(\Delta\rho)^2 \lambda^2 t}\right)}}{2} \qquad (7)$$

and the solvent volume fraction $\phi_{sol}=1-\phi_{agg}$ for a binary system. In order to convert this to solubility we use the following simple equation:

$$Solubility = C_{solution} - \left(\phi_{agg}\, d_{PCBM}\right) \qquad (8)$$

, where $C_{solution}$ is the total concentration of $PC_{61}BM$ in solution (30, 60 or 90 mg.mL^{-1}), and d_{PC61BM} is the density of $PC_{61}BM$ which we consider as 1500 mg.mL^{-1}.

	Density g·cm^{-3}	SLD (Å^{-2})
PC$_{61}$BM	1.5[a]	4.34x10^{-6}
PC$_{71}$BM	1.5[a]	4.42x10^{-6}
Chloroform	1.49	2.36x10^{-6}
Toluene	0.87	0.94x10^{-6}
Chlorobenzene	1.11	1.82x10^{-6}
DIO	1.84	0.12x10^{-6}

Table S1. Densities and neutron scattering length densities of the fullerenes and solvents used in this study. [a][Kiel, J. W., Eberle, A. P. R. & Mackay, M. E. Nanoparticle Agglomeration in Polymer-Based Solar Cells. Physical Review Letters 105, 168701 (2010)]
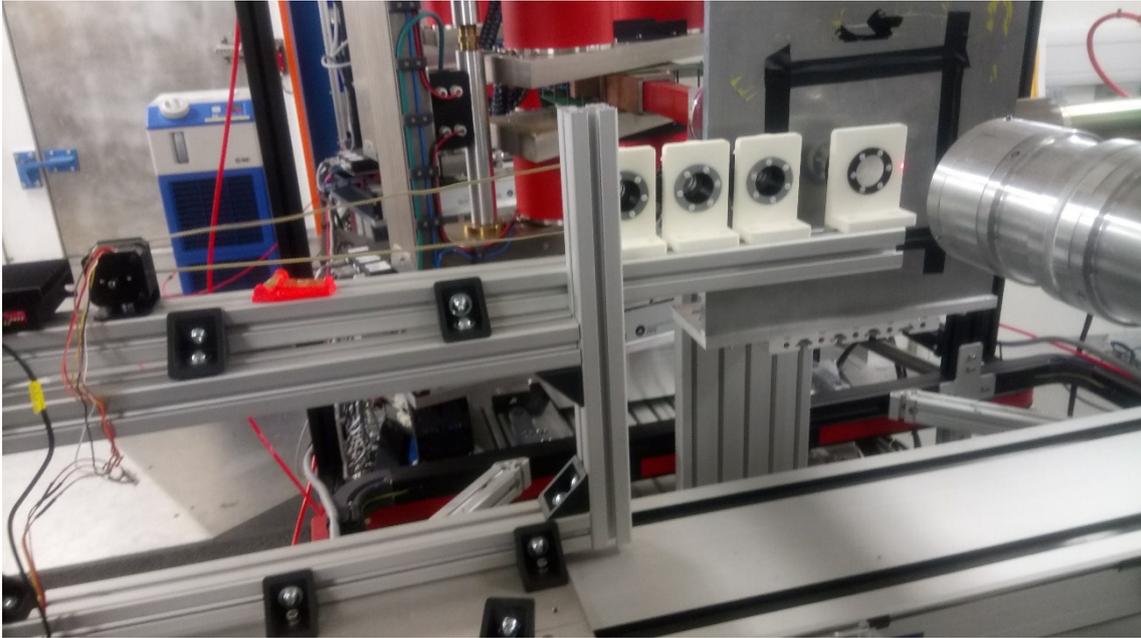
Figure S1. Rotation apparatus, with cell holders made of Teflon, placed in the beamline

	PC$_{61}$BM	PC$_{71}$BM
Chloroform	30 mg·mL^{-1} 	90 mg·mL^{-1}
Toluene	60 mg·mL^{-1} 	90 mg·mL^{-1}
Chlorobenzene	90 mg·mL^{-1} 	90 mg·mL^{-1}
DIO	90 mg·mL^{-1} 	90 mg·mL^{-1}
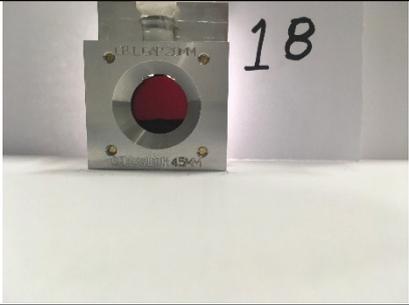
Figure S2. Photos of solutions after ~48 h at rest. We note that, due to the high fullerene concentrations ($\geq$ 30 mg·mL^{-1}) and cell path lengths (1 mm) used, at the time of the SESANS measurements all the solutions were completely opaque (and macroscopically homogeneous). After ~48 hours at rest (photos shown), all the PC$_{71}$BM solutions remained completely opaque and macroscopically homogeneous (including those with 90 mg·mL^{-1}) but most of the PC$_{61}$BM solutions had suffered large phase segregation.
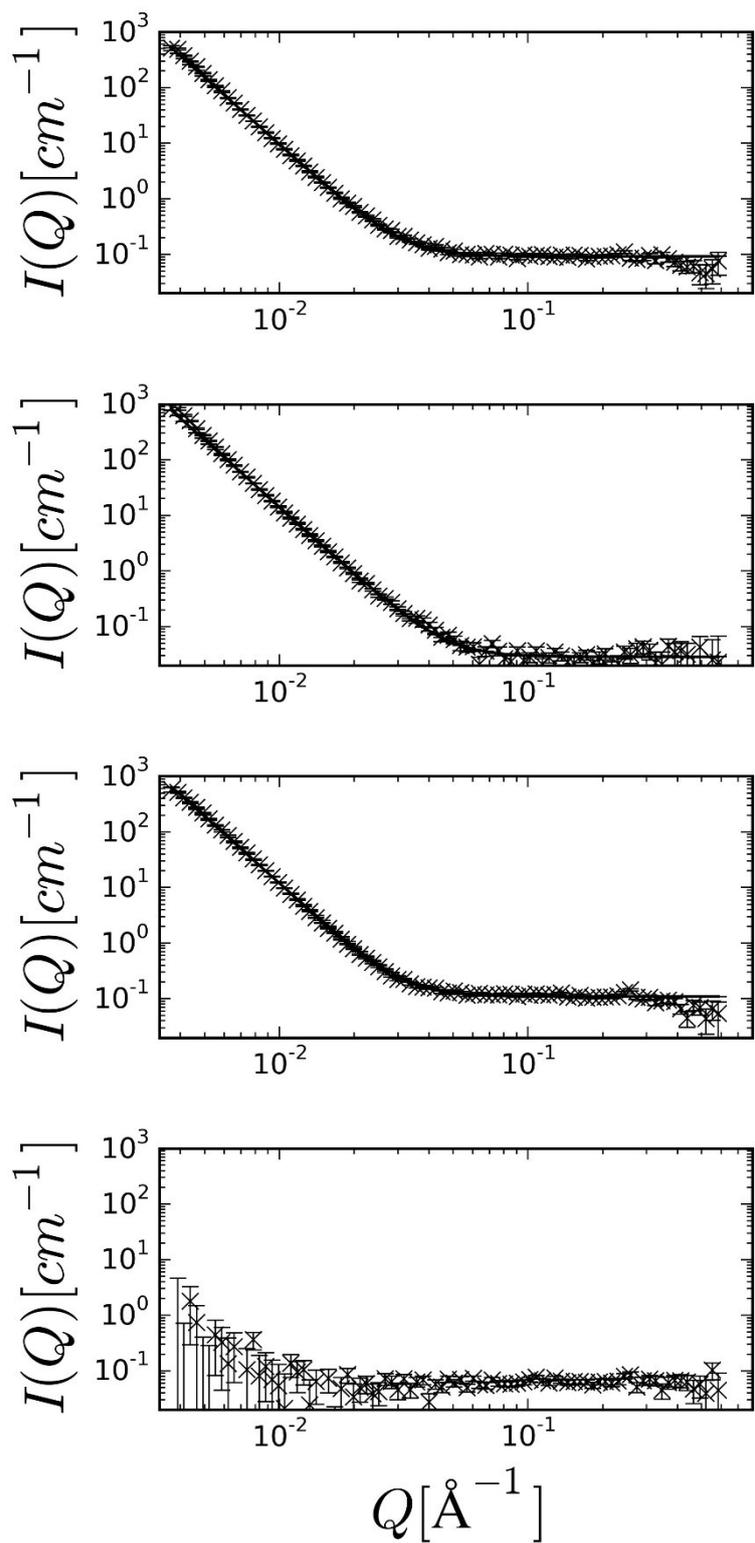
Figure S3. SANS results of (top to bottom): $PC_{61}BM$ in DIO (90 mg·mL^{-1}); $PC_{61}BM$ in Chlorobenzene (90 mg·mL^{-1}); $PC_{71}BM$ in Toluene (90 mg·mL^{-1}) and $PC_{61}BM$ in Chlorobenzene (30 mg·mL^{-1}).