Supporting information

Polymer mediated assembly of fullerenes into non-closed packed two-dimensional arrays

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Experimental

Materials: De-ionized water (resistivity of 18.3 mΩ), toluene (Gadot, Israel 99.8%), [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) (99%, Solenne BV, the Netherlands), poly(ethylene glycol) PEO-10K M_n =10,000 (Aldrich), F127 ($PEO_{100}PPO_{65}PEO_{100}$) and 25R4 ($PPO_{32}PEO_{36}PPO_{32}$) (BASF), Poly(styrene-b-ethylene oxide) ($PS_{35}PEO_{1520}$) (Polymer source, Inc.) were used as received.

Spreading solutions: Spreading was carried out from toluene solutions of the relevant block-copolymers (F127 1 wt%, 25R4 0.3, 1, 1.77 wt% or PEO-PS 1 wt%) and PCBM (1.5 mg/ml). The typical dimensions R_g are PEO (water) ~ 4.5nm, F127 (toluene) ~4nm, 25R4 (toluene) ~0.5 nm.

Surface tension measurements: The surface tension of the solutions was characterized using De-Nouy ring tensiometer (model sigma 701, KSV Instruments Ltd.) at lifting speed of 1 mm/min, and an ambient temperature of 21 °C.

Experimental setup: A computerized Langmuir trough (model 622/D1, Nima Technology Ltd, Coventry, UK) with effective area between 545 - 70 cm^2 was used. The spreading solution was placed drop-wise on the subphase. The carrier solvent was allowed to evaporate completely before in-situ characterization was carried out.

In-situ characterization: BAM (NFT, Gottingen, Germany) mounted on a Langmuir film balance was used for surface characterization. A frequency-doubled Nd:YAG laser with a wavelength of 532 nm and 50 mW primary output power in a collimated beam was used for imaging, and the resulting images were recorded via a CCD camera. A scanner objective (Nikon) of a nominal 10× magnification and diffraction-limited lateral resolution of 2 µm was used.

Ex-situ characterization: Ex-situ characterization was applied to samples prepared using the Langmuir-Schaefer method (*horizontal* lift). Glass (cover slip, Mensel-Glaser, Germany) or silicon wafers were used as substrates. The samples were characterized using Atomic Force Microscopy (AFM Dimension 3100, Veeco, U.S.A.) and scanning electron microscopy (SEM, JEOL JSM-7400F). Samples for SEM were gold coated.

Optical Phase Interference Microscopy (OPIM, New View 200, Zygo, USA), OPIM, was used for profiling patterns of NP transferred onto glass and mica. The set up used in this study offers sub-nanometric resolution in the vertical direction, a lateral resolution of 0.64 mm, and a maximal field of view of 280x220 mm^2. In this technique a beam of white light that scans the sample is reflected from the surface and interferes with a reference beam, to generate an interference pattern that is monitored by a CCD camera. The pattern is analyzed using a computerized algorithm ("frequency domain analysis") to obtain a quantitative 3-D image of the sample.
UV-vis measurements were carried out using V530 spectrophotometer (Jasco japan).

The spreading coefficient S = $\gamma_{aqu/air}-\gamma_{tol/air}-\gamma_{tol/aqu}$ *mN/m*, where $\gamma_{aqu/air}$ is the interfacial tension at the aqueous subphase-air interface, $\gamma_{\text{tol/air}}$ is the interfacial tension of the relevant spreading solution and $\gamma_{\text{aqu/tol}}$ is the interfacial tension at the relevant aqueous subphase and the spreading solution interface. In Table S1 we present calculated values of the spreading coefficient for relevant combinations of the subphase and the spreading solution. The calculated values indicate that at all the relevant combinations the spreading coefficient is positive and evaporation drives the toluene solutions towards spreading, and a wetting transition (from "wetting" to "dewetting") does not take place under the experimental conditions.

Table S1: Calculated values of the spreading coefficient, S

Subphase	Spreading solution (toluene)	$\gamma_{\text{tol/air}}$ [mN/m] ± 0.5	$\gamma_{\text{subphase/ tol-sol}}$ [mN/m] ± 0.5	Calculated spreading coefficient [mN/m]
Water	Toluene	28	36	8
Water	F127 (1 wt%)	27	<36.5	>9
Water	25R4 (1 wt%)	27	< 36	>10

$\gamma_{\text{tol/air}}$ is the interfacial tension of the relevant spreading solution (in toluene)
$\gamma_{\text{aqu/tol}}$ is the interfacial tension between the relevant aqueous subphase and the spreading solution.

The measured water/air interfacial tension 72 ± 0.5 mN/m (at 21 °C).

UV-vis measurements (Fig.S1) of samples prepared under conditions similar to those presented in Fig.1 b, and collected on a quartz substrate indicate that the sample is composed of a mixture of PCBM and F127. We note that the absorption pattern of PCBM resembles that of PCBM in solution rather than that observed in films of closely packed PCBM.[1]

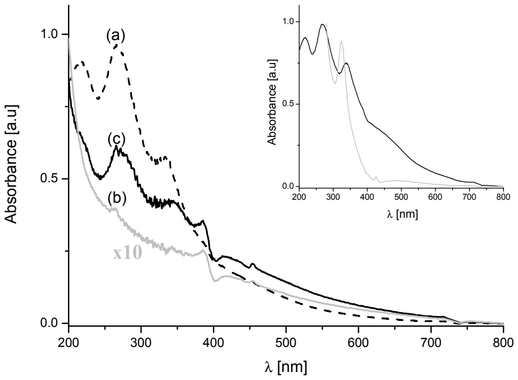

Figure S1: UV-vis absorption spectra of thin films prepared by collecting 10 layers from the water-air interface onto a quartz substrate. (a) PCBM film (from a toluene solution) (b) F127 film (from a toluene solution) (c) a sample of PCBM-F127 as in Fig.1 c. The inset: PCBM in toluene solution (grey), a PCBM film spin-coated from toluene solution (black).

A histograms presenting the distribution of cell diameters in networks formed by PCBM –25R4 –toluene solutions of PCBM: 25R4 of molar ratio 1 : 1.68

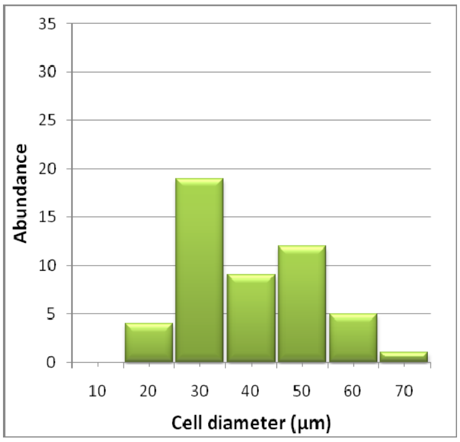

Figure S2. A histograms presenting the distribution of cell diameters in networks formed by PCBM –25R4 – toluene solutions (PCBM: 25R4 molar ratio 1 : 1.68) at initial area per NP of 2.75 nm^2 on a water subphase, with a mean cell diameter of 39 microns and a standard deviation of 12.5. The cell diameter was measured by fitting a circle to BAM images of the networks, collected *in-situ* at the solution-air interface.

To test the effect of the polymer-NP ratio on the formed patterns we carried out two additional experiments, at a polymer; NP molar ratio of 1:3 Fig. S3 (a,b) and 1:0.5 Fig.S3 (c,d). We observe the formation of denser networks of PCBM when the polymer concentration is increased to (with a typical cell diameter of 20 microns), while low polymer-NP ratio (Figure S3c,d) does not lead to the formation of a percolating network of NP cells. These observations suggest that there exists a minimal polymer –NP ratio necessary for the formation of a connected network of aggregated NP.

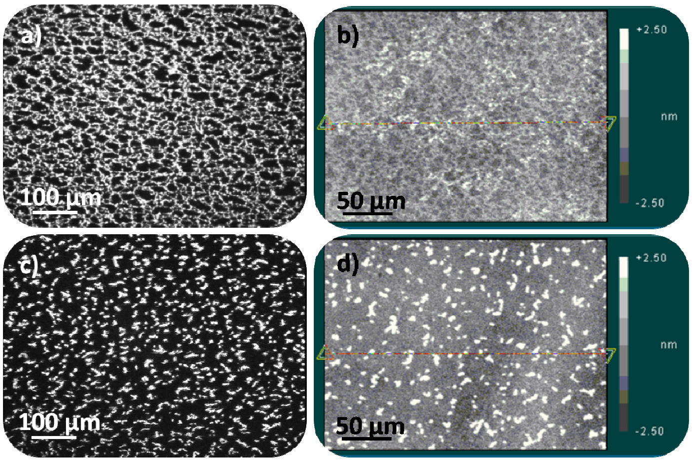

Figure S3 *(a)In-situ* BAM image of arrays formed at the water-air interface following complete evaporation of the carrier solvent (toluene) from a solution of PCBM and 25R4, at initial area per NP of. 2.75nm^2 and a PCBM: 25R4 molar ratio of 1:3 b) An OPIM images of a smaple transferred onto a glass substrate c) *In-situ* BAM image of a PCBM:25R4 in toluene prepared as (a) but at a PCBM-25R4 molar ratio of 1: 0.5 d) An OPIM image of (c) transferred onto a glass substrate.

References

1. S. Cook H. Ohkita Y. Kim J. J. Benson-Smith D.D.C. Bradley J. R. Durrant *Chem.Phys. Lett*. 2007, **445**, 276.