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

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Polymer-mediated depletion interactions were found to induce the assembly of fullerene derivates at the water–air interface into non-closed-packed 2-dimensional arrays of nanometric thickness.

Synthetic superstructures of functional nanoparticles (NP) were shown to exhibit novel collective properties[1] suggesting large potential in applications such as data storage, control of photonic band gaps, chemical sensing,[2,3] smart coatings and more. A major challenge in most applications is to design the optimal morphology and engineer the assembly[4,5] of the NP into thermodynamically stable or non-equilibrium long-lived structures.

When the building blocks of the desired structures are spherical nanoparticles (whether metallic or dielectric) the thermodynamically stable morphology of planar arrays is mostly dense, close-packed superlattice,[6–8] though some exceptions were suggested.[9] Yet, non-closed-packed (ncp) two-dimensional networks of nanoparticles may be desired when aiming to design multi-functional materials or devices, such as transparent-and-conducting coatings. In the latter case, cellular networks of NP that offer a connected pathway for conductivity while not affecting the transparency of a target substrate are much desired. Among the more useful nanoparticles are fullerenes and fullerene derivatives such as [6,6]-phenyl-C_{61}-butyric acid methyl ester, PCBM. These serve as the electron accepting phase when mixed with conjugated polymers in organic photovoltaics.[10] The small diameter of $\sim$1 nm that characterizes fullerene NP, their monodispersity and hydrophobicity mostly drive the NP into close packed structures while ncp morphologies are hard to obtain.[11,12]

Here we show that non-adsorbing block-copolymers may be used for inducing the assembly of two-dimensional (2-D) ncp arrays of fullerenes at the water–air interface. In our experiments a polymer–NP mixture is prepared in a volatile organic solvent which dissolves both the NP and the polymer, and the organic solution is spread[13] at the water surface. Following the spreading and partial evaporation of the solvent, re-arrangement of the NP at the air–water interface takes place due to the interaction between the NP and the non-adsorbing polymers leading to the formation of arrays of different morphologies.

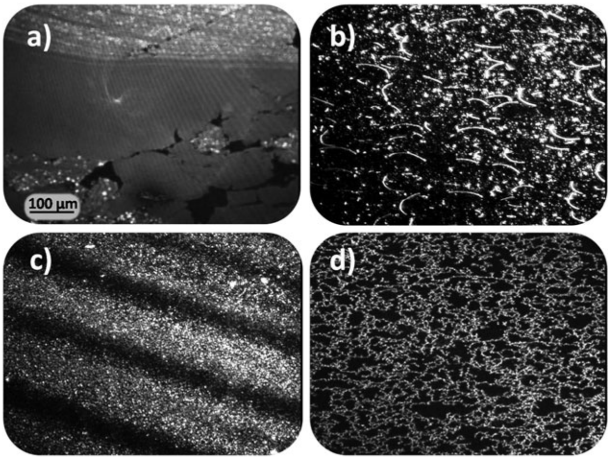
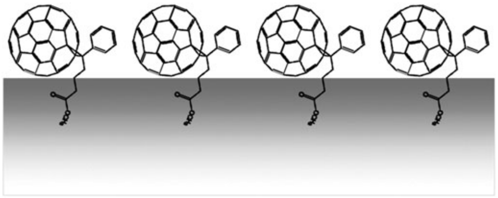


Fig. 1 *In situ* BAM images of the structures formed following complete evaporation of the carrier solvent (toluene) at the water–air interface. (a) PCBM in toluene. (b) A toluene solution of PCBM–F127 (molar ratio of PCBM to F127 of 1 : 0.48) at a calculated (initial) surface area per PCBM NP of 2.75 nm^2. (c) Same as (b), but the subphase is a PEO solution (1 wt%). (d) A toluene solution of PCBM–25R4 (molar ratio of PCBM to 25R4 of 1 : 1.68) at a calculated (initial) surface area per PCBM NP of 2.75 nm^2. Regions of high NP concentration appear bright while polymer rich regions are dark.

In Fig. 1b–d, we present *in situ* Brewster Angle Microscope (BAM) images of NP arrays formed following the spreading of PCBM NP from a polymer solution at the water–air interface. Fig. 1a, presented for comparison, shows a densely packed film of PCBM NP which forms in the absence of a polymer. The aggregation of the NP is irreversible and the structure is similar to that reported in previous studies of similar fullerene derivatives at the water–air interface[14] where it was suggested that the NP orient with the hydrophilic moiety towards the water phase (Scheme 1).

Addition of the amphiphilic block copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), PEO_{106}–PPO_{70}–PEO_{106} F127 (BASF, M_n = 12 600 g mol^{-1}, $R_g \approx 4$ nm[15] in toluene) or PPO_{32}–PEO_{36}–PPO_{32} 25R4 (BASF M_n = 3600 g mol^{-1}, $R_g \approx 0.5$ nm in toluene) to the spreading



Scheme 1 A schematic presenting a probable configuration of the PCBM NP at the aqueous solution–air interface (following ref. 14).

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solution results in the morphologies presented in Fig. 1b–d. Due to the presence of the polymer the close packed pattern of Fig. 1a is replaced by ncp morphologies: micron-sized filaments, stripes and networks of polygonal cells (*Voronoi cell structures*[16]) are observed (Fig. 1b–d). The meso-scale morphology of the resulting arrays is also affected by the presence of a homopolymer (poly(ethylene oxide), PEO) in the subphase (Fig. 1c).

UV-vis measurements (Fig. S1, ESI†) of samples prepared under conditions similar to those presented in Fig. 1b, and collected on a quartz substrate indicate that the sample is composed of a mixture of PCBM and F127. Furthermore, the absorption pattern of PCBM resembles that of PCBM in solution rather than that observed in films of closely packed PCBM.[17]

The observed patterns are long-lived, and may be trapped and transferred onto different substrates with a high degree of fidelity as presented in Fig. 2. *Ex situ* structural analysis of networks (Fig. 1d) transferred from the water–air interface onto glass substrates *via* Atomic Force Microscopy (AFM, Fig. 2a and b) shows the typical network structure. A higher magnification (Fig. 2c) reveals that the cell walls are composed of a network of cells of similar height but much smaller lateral dimensions in the range of some tens of nanometres. A height (thickness) of few <4nm (Fig. 2e OPIM) nanometres, and a typical cell diameter of 39 microns (for statistical analysis see the ESI†, Fig. S2) are observed.

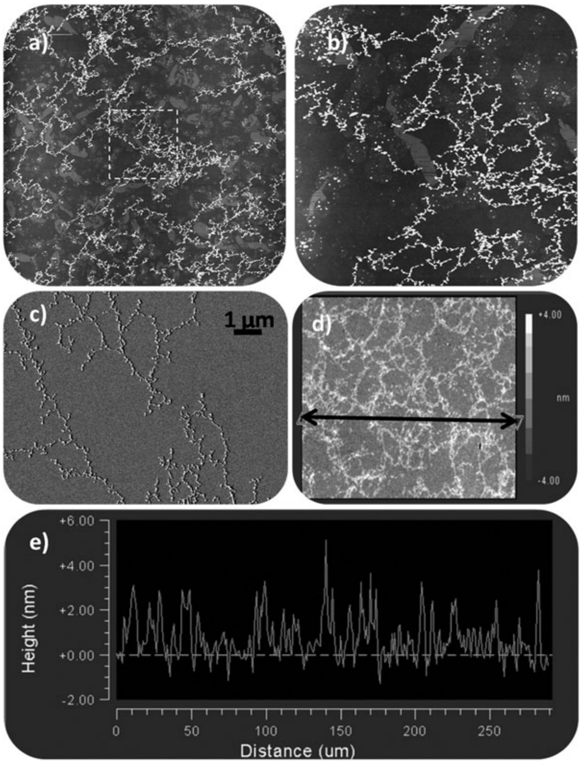

Fig. 2 Images of PCBM assemblies formed following the spreading of a PCBM–25R4–toluene solution at the air–aqueous solution interface at 2.75 nm^2 per NP, and PCBM : 25R4 molar ratio of 1 : 1.68, transferred onto a glass substrate: (a) Atomic Force Microscope (AFM) image 80 × 80 μm. (b) Larger magnification of the marked area at (a), image size 20 × 20 μm. (c) High resolution Scanning Electron Microscope (SEM) image. (d) and (e) OPIM image and a profile taken along the line.

We found that the networks can withstand external pressure: the barriers of a Langmuir trough were used to apply lateral pressure on the surface structures, and compress the networks. The *in situ* BAM images (Fig. 3a–e) clearly show that the networks respond to compression and de-compression by contraction and expansion of the cells, while preserving the network morphology and the surface structures. We suggest that the 2-D elasticity of the structures probably results from the multi-scale structure of the cell-walls (Fig. 2a–c).

In all the systems described here, the formation of the observed structures may result from entropic interactions between the co-dissolved block-copolymers and the NP, known as depletion interactions.[16] In the suggested scenario, assembly is initiated by solvent evaporation which effectively increases the concentration of the components and triggers depletion interactions. These drive the system towards phase separation at the interface. When the co-dissolved block copolymer (F127) is soluble in the subphase, a slow process of polymer dissolution follows leaving behind the non-soluble NP. Both solvent evaporation and polymer dissolution are slow (minutes and about an hour, respectively) on the time scale of the particles and polymers in-plane diffusion. Thus, the growing domains re-arrange under the combined interactions leading to the formation of the steady-state patterns presented here.

Rabani *et al.*[18,19] suggested that in such systems solvent evaporation triggers the onset of NP coarsening while the growth mechanism and the resulting transient patterns are

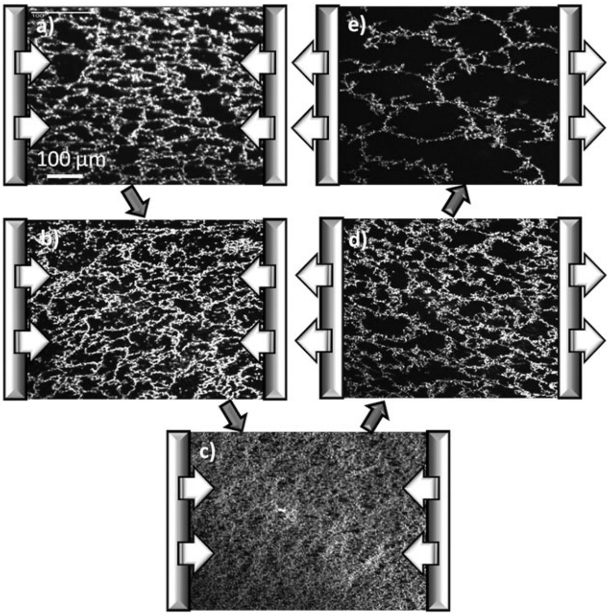

Fig. 3 *In situ* BAM images of a compression process in a Langmuir trough of a PCBM network at the air–water interface. The network assembled spontaneously from a PCBM–25R4–toluene solution with a PCBM : 25R4 molar ratio of 1 : 1.68. and the smallest area per molecule (c) is 0.35 nm^2. Compression (a–c), de-compression (d and e). The scale bar applies to all the images. The initial area per NP (a) is 2.75 nm^2.

shaped by the sequence and details of the evaporation mechanism.[18,19]

Depletion interactions were first described by Asakura and Oosawa[20] and thoroughly studied in the context of colloidal dispersions.[21] Following their description, entropic interactions in a mixture of dispersed spheres of radius R_{large} and R_{small} where ($R_{\mathrm{large}} \gg R_{\mathrm{small}}$) lead to expulsion of the small spheres from the region between two large spheres. The consequential osmotic pressure gradient leads to crowding of the larger spheres thus increasing the free volume available to the smaller spheres and consequentially decreasing the overall free energy of the combined system. The interaction may be described as an effective attraction between the larger spheres with a potential well of approximately $\sim 3/2(R_{\mathrm{large}}/R_{\mathrm{small}})\phi_{\mathrm{small}}k_{\mathrm{B}}T$, where ϕ_{small} is the volume fraction of the small particles, and $k_{\mathrm{B}}T$ is the thermal energy. The small diameter of PCBM NP allows us to explore two different regimes: in the first, where the R_{g} of the polymer is larger than that of the NP (F127, $R_{\mathrm{g}} \sim 4$ nm) depletion interaction drives the polymers towards crowding into filaments or stripes. As the polymer is soluble in the sub-phase islands of the non-soluble component (the PCBM) are left at the water–air interface (Fig. 1b) and their lateral distribution is affected by the solvated polymer (Fig. 1c), probably due to entropic repulsion, in this case between the solvated and surface polymers. In the second scenario described here (Fig. 1d), the polymer (25R4) is insoluble in water, and $R_{\mathrm{g}} < 0.5$ nm. Thus the PCBM NP of diameter ~ 1 nm experience an imbalanced entropic pressure that leads to effective depletion-induced attraction among the NP. The particles are pushed towards the boundaries of the polymer patches forming a cellular network. Though the patterns presented here may not represent equilibrium structures, the observed morphologies are found to depend on the ratio between the gyration radius of the polymer, R_{g}[16], to the NP diameter and the relative polymer: PCBM concentration. A high sensitivity of the formed structures to the relative concentration of the polymer and the NP is demonstrated in the results detailed in Fig. S3 of the ESI.†

To conclude, we suggest that non-specific depletion interactions may be utilized for the design and preparation of 2-D arrays of non-closed packed NP at the water–air interface. In this approach one may make use of a large variety of commercially available block-polymers for surface engineering of 2-D arrays of NP. Moreover, the use of a non-adsorbing polymer as a structure-mediating agent offers an advantage for applications that rely on the electronic and optical properties of the intrinsic properties of the native, unaltered NP (electron affinity, absorption, emission).

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