Cross-conjugated poly(*p*-phenylene) aided supramolecular self-organization of fullerene nanocrystallites†

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Formation and characterization of nanocrystallite spheres from a hybrid of functionalized cross-conjugated poly(*p*-phenylene) and C_{60} are reported.

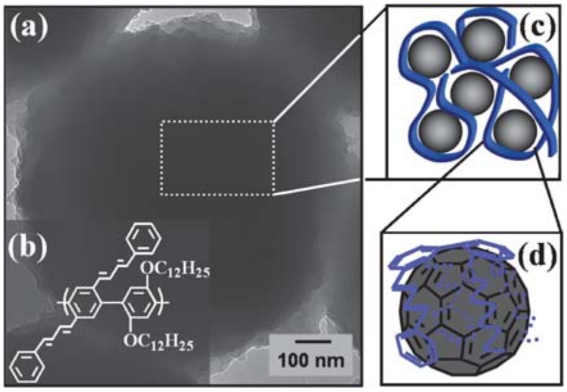

Fig. 1 TEM micrograph of 1 : 1 blend of C_{12}-XPPP–C_{60} hybrid nanocrystallites prepared in 0.1 mg mL^{-1} toluene solution (a) with inset showing the molecular structure of the polymer (b) and the proposed mechanism of formation (c–d).

Many current and a new generation of optical and electronic organic materials are primarily conjugated.[1] Polymers that are extensively conjugated are significantly explored due to the tunability of their properties through variation of their chemical structure. However, efficiencies of polymer-based devices are mainly limited by the short exciton diffusion lengths of polymers.[2] Substantial improvement in efficiencies of energy conversion can be achieved at interfaces of materials with different electron affinities[3] and the discovery of photo-induced electron transfer from the excited state of the conjugated polymer to fullerene (C_{60}) opened a new route to applications.[4]

The poor solubility and strong aggregation of C_{60}s led to the design and synthesis of a number of new C_{60} derivatives,[5] with high solubility. Developing efficient methods to form consistently uniform crystals by spontaneous self-assembly is crucial for the exploitation of C_{60}s in photovoltaic (PV) applications[6] and studies in microbial response of C_{60} clusters.[7] In an effort to induce enhanced interactions between C_{60} and polymer matrices, we previously utilized an amphiphilic poly(*p*-phenylene) for a room temperature stabilization of hybrid nanofibers without the need for high temperature annealing or for covalent functionalizations of C_{60}.[8]

In the studies described here, a two-dimensional (2D) orthogonally conjugated polymer (Fig. 1b) was used as a donor (see Supporting Information **S1** for synthetic details†) and C_{60} as an acceptor to form a homogeneous blend. A convenient methodology to control the morphology of nanocrystallites from C_{60} and the 2D conjugated polymer is given in full detail. The 2D conjugated polymer has a conjugated backbone as well as conjugated side chains on every alternate ring. Studies have shown that the cross-conjugation contributes to the overall π-electron delocalization.[9] There is also co-existence of strong π–π stacking among 2D conjugated polymer molecules, which is comparatively weaker in 1D conjugated polymers.[10] This increased conjugation in the 2D aromatic network is also advantageous in dispersing the C_{60}s and for PV applications due to the higher electron density that can be transferred to C_{60}, leading to an enhanced charge generation and hole mobility.[11]

Since interchromophoric order is crucial for efficient functioning of organic electronic devices, two- and three-dimensional nanostructured ordering in bicontinuous materials becomes fundamental. A significant breakthrough has been achieved by realising that the morphology of the composites plays an important role in device performance[12] and understanding the contribution of the morphology to the physical properties. C_{60}

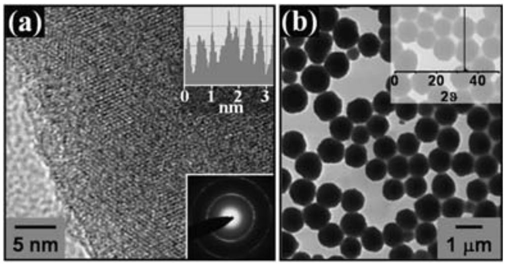

Fig. 2 High resolution TEM micrograph (a) of 1 : 1 blend of C_{12}-XPPP–C_{60} hybrid nanocrystallites prepared in 0.1 mg mL^{-1} toluene solution. The inter-lattice spacing measurement is in the upper inset and electron diffraction in the lower inset. The corresponding low magnification TEM (b) with an X-ray diffractogram in the inset shows monodispersed particles.

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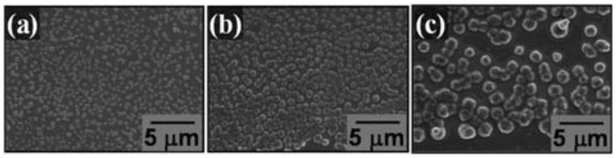

Fig. 3 SEM images of C_{60}–C_{12}-XPPP 1 : 1 blend in toluene at 0.1 mg mL^{-1} (a), 0.2 mg mL^{-1} (b), 0.5 mg mL^{-1} (c).

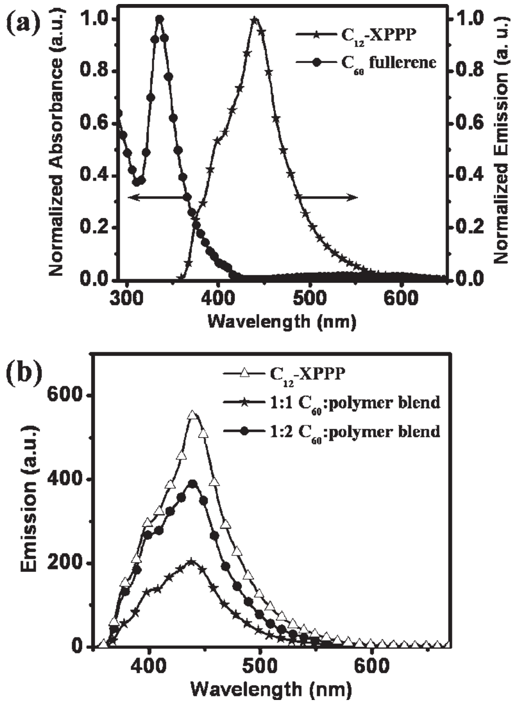

Fig. 4 Respective absorbance and fluorescence emission of individual components (a), and quenching of emission (b) of C_{12}XPPP with C_{60} blends.

crystallized from toluene solution gave non-uniform rods while the polymer formed a featureless uniform film when cast from the same solvent (see Supporting Information **S2**†). Addition of C_{60} into the 0.1 wt% polymer solution in a 1 : 1 blend caused substantial changes in morphology. Nanocrystallites of the blend with uniform sized spheres were observed (Fig. 2). The presence of aromatic groups on both the backbone and side chains facilitated the dispersion of C_{60} and directed the π–π interaction driven co-assembly (Fig. 1c–d).

In addition, there were no visible phase separated C_{60} aggregates in the nanocrystallites and well-defined lattice fringes were observed in the high resolution TEM image (Fig. 2a). The inter-lattice spacing measured here as well as in X-ray diffraction averages 0.3 nm, which is in agreement with the side chain end-to-end distance within the polymer packing.[13]

As determined in previous studies, parameters such as casting solvent, concentration and composition of the polymer and C_{60} in the nanohybrid significantly influence the morphology.[14] The dynamics of solvent evaporation play a vital role in crystallization behavior and morphology of the nanohybrid. Under conditions of fast solvent evaporation, *i.e.* through spin coating, densely and homogeneously distributed nanospheres were formed. Sizes of the spheres decreased as the solvent evaporation rate was increased. In contrast, when the solvent evaporation rate is reduced, *i.e.* through drop casting, spheres with size on the order of micrometres are formed (see Supporting Information **S3**†).

To investigate the influence of concentration on morphology, solutions of different concentrations, but with constant ratio (1 : 1) between C_{60} and C_{12}-XPPP, were prepared and drop cast from toluene solutions. The SEM images revealed that varying the solution concentration of the C_{60}–C_{12}-XPPP blend did not hinder the formation of the spherical nanocrystallites. As shown in Fig. 3, films of the blend consisting of spherical structures were formed. Upon using a 0.1 mg mL^{-1} solution, crystallites with an average size of 200 nm were obtained, while those prepared using the 0.2 mg mL^{-1} and 0.5 mg mL^{-1} solutions led to spherical particles with a size of 500 nm and 1200 nm, respectively. Moreover, with a lower concentration, the spherical domains had a smaller size distribution and were more uniformly dispersed throughout the film (see Supporting Information **S4**†).

Inter-chromophore order and homogenous dispersion of the donor–acceptor system are essential for efficient performance of materials in applications such as organic electronics.[15] It is further validated in the changes observed in photophysical properties of the blend. With absorption in the ultraviolet region, C_{60} has significant overlap with the emission of the polymer (Fig. 4a). As a consequence, photoluminescence was quenched by photoinduced electron/energy transfer with an intimate mixing of the donor–acceptor interface. (UV absorbance of the polymer and blend is shown in Supporting Information **S5**†). As shown in Fig. 4b, 31% quenching was observed in the 1 : 2 C_{60}–polymer blend and 64% in the 1 : 1 C_{60}–polymer blends in toluene.

Here we show a significant structural control of nanocrystallites from a cross-conjugated polymer with C_{60} using a conventional drop casting method. In line with previous nanohybrid studies, where PPP backbones were engineered with hydroxyl groups and single[8] or double[16] long alkoxy chains on every repeat unit, significant inter-component interactions were observed in the present system. Strong π–π interactions between the polymer and C_{60}s, coupled with the weak interactions of the dodecyloxy chains, guided the self-assembly to uniformly sized nanocrystallites. The aggregate size and dispersions were tailored and studied. Extensive photophysical and photocurrent studies of the hybrids are underway.

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