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Structural dynamics and charge transfer via complexation with fullerene in large area conjugated polymer honeycomb thin films[†]

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Ordered microporous polymer surfaces have attracted substantial interest because of their potential applications in biocatalysis,[1,2] mesoporous materials,[3−5] superhydrophobic surfaces,[5,6] and optoelectronics.[7,8] Since the first report demonstrating self-assembly of honeycomb frameworks from star-shaped polystyrene and poly(para-phenylene)-block-polystyrene,[9] similar honeycomb-patterned structures using various kinds of polymeric materials have also been realized.[10,11] Of particular interest is the incorporation of conjugated polymer components such as poly (phenylene vinylene)-*b*-polystyrene (PPV-b-PS) block copolymer[7,12] or hyperbranch PPVs[13,14] into honeycombs to render electronic and optical properties that can be useful for solar and optoelectronic devices.[10]

Here we demonstrate the fabrication and detailed characterization of honeycomb structures based on a functionalized PPV, poly{2,5-bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-1,4-phenylenevinylene} (P1, Figure 1a), using the breath-figure technique (BFT).[10,15−17] This conjugated polymer of low molecular weight (10.5 kDa), when dissolved in chlorobenzene, features absorption and photoluminescence (PL) spectra peaking at 503 and 565 nm, respectively (see Figure S1 in the Supporting Information), and a PL quantum yield of 0.2.[18] Herein we report structural and optical properties of P1-based honeycomb and demonstrate charge transfer when the honeycomb is complexed with fullerenes (Figure 1a), either by electrostatic interaction (P1/C$_{60}$ honeycomb heterojunction) or in blend.

The BFT mechanism is depicted in Figure 1a. It relies on the condensation of micrometer sized water droplets on a polymer solution surface. As the solvent evaporates, the void space created by the water droplets allows formation of a regularly packed honeycomb structure driven by capillary forces. P1-honeycombs prepared from chlorobenzene exhibit structure regularity over extremely large areas (up to 1 mm^2). Scanning electron microscopy (SEM) imaging (Figure 1b) illustrates a highly regular honeycomb framework patterned over large scales (>200 μm), consisting of perfect hexagons with 3−4 μm size. In contrast, the as-cast P1 film is featureless with respect to any framework (see Figure S2a in the Supporting Information).

The polymer concentration used for BFT plays a dominant role in determining the final morphology of the honeycomb structure: an ideal concentration of 4 mg/mL leads to a highly uniform honeycomb structure (Figure 1b−d, Figure S3d in the Supporting Information), whereas higher concentration (>6 mg/mL) results in a thick film with rounded holes (see Figure S3a in the Supporting Information). A lower concentration (<2 mg) gives rise to defects and eventually unconnected individual ring structures (see Figure S3e,f in the Supporting Information). For P1-honeycomb, defects in the form of pentagons and heptagons are present, though they represent less than 1% of the structure. P1-honeycombs are highly tranparent at the center of the hexagon rings when observed in optical transmission microscopy (Figure.1c) and highly fluorescent when observed with an epifluorescence microscope under blue light (Figure.1d). Analysis of P1-honeycomb surface morphology by atomic force microscopy (AFM) reveals average node/frame thicknesses of 600 nm/250 nm, respectively (see Figure S3 in the Supporting Information).

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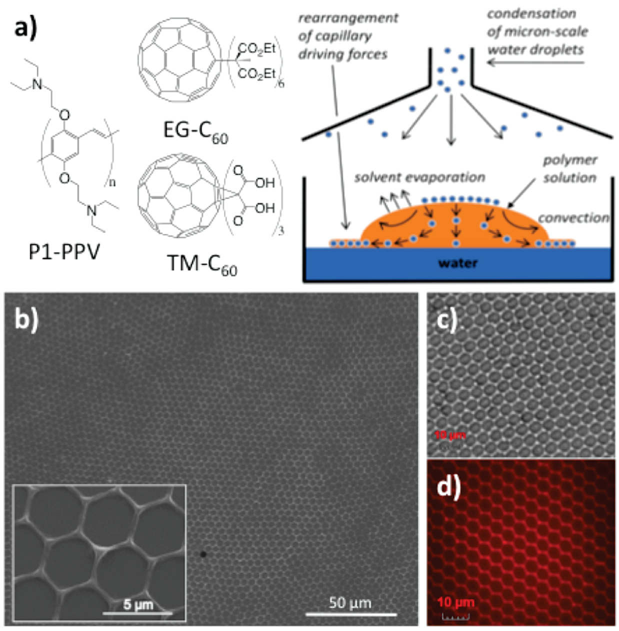

Figure 1. (a) Structures of P1, of water-soluble trismalonic fullerene (TM-C_{60}) and emerald fullerene (EG-C_{60}). Schematic illustration of the breath method used to deposit large area (up to 1 mm^2) P1-honeycombs. (b) SEM image and zoom of a P1-honeycomb deposited from chlorobenzene. (c, d) Optical bright-field and fluorescence images of a P1-honeycomb deposited on a coverglass.

To understand how the honeycomb structure impacts the optical properties of P1, we compared the optical properties of a P1-honeycomb film prepared by BFT and one prepared by drop-casting a P1 film from chlorobenzene using confocal fluorescence lifetime imaging (FLIM) and microspectroscopy (see method details in the Supporting Information). For the as-cast film, the PL intensity is relatively homogeneous across the film (Figure 2a), with a relatively long PL lifetime (1.5 ns on average, see Figure 2c and Table 1), except for a few small spots that are brighter in intensity and exhibit a shorter lifetimes (0.5−0.6 ns), presumably corresponding to aggreagates. The PL decay from a diffraction-limited spot located in the homogeneous region of the sample (region (1) in Figure 2c) is biexponential with lifetimes (contributions) of 1.9 ns (42%) and 0.57 ns (58%). The corresponding diffraction-limited PL spectrum (Figure 2e, black curve) resembles the PL spectrum of P1 polymer in chlorobenzene.

For P1-honeycomb, intense PL signals are detected only from hexagon frameworks and in particular from the intersection points or nodes on the framework (Figure 2b). These regions feature PL lifetimes, on average of 0.43 ns (See Figure 2d and Table 1). Specifically, diffraction-limited PL decays measured from rings and nodes (Figure 2d, regions 2 and 3) are biexponential, with lifetimes (contributions) of 0.90 ns (20%) and 0.25 ns (80%) for the frame (Figure 2f, curve 2) and 0.83 ns (13%) and 0.23 ns (87%) for the nodes (Figure 2f, curve 3). The associated PL spectra (Figure.2e, red curve) are red-shifted (peak at 600 nm) and vibronically structured. This photophysical behavior, including the vibronically resolved red-shifted emission, is very similar to that previously observed for structured aggregates of polymer P1 at room temperature in toluene,[19] suggesting that similar structures are likely formed here. Similar vibronically structured, red-shifted PL spectra have also been observed for other conjugated polymers and associated with aggregates exhibiting highly ordered regions with an extended chain conformation which favors enhanced $\pi-\pi$ stacking.[19−21] Thus, taken together, these experimental data suggest that regions of ordered polymer aggregates exist in the honeycomb framework, leading to extended conjugation lengths and red-shifted emission.

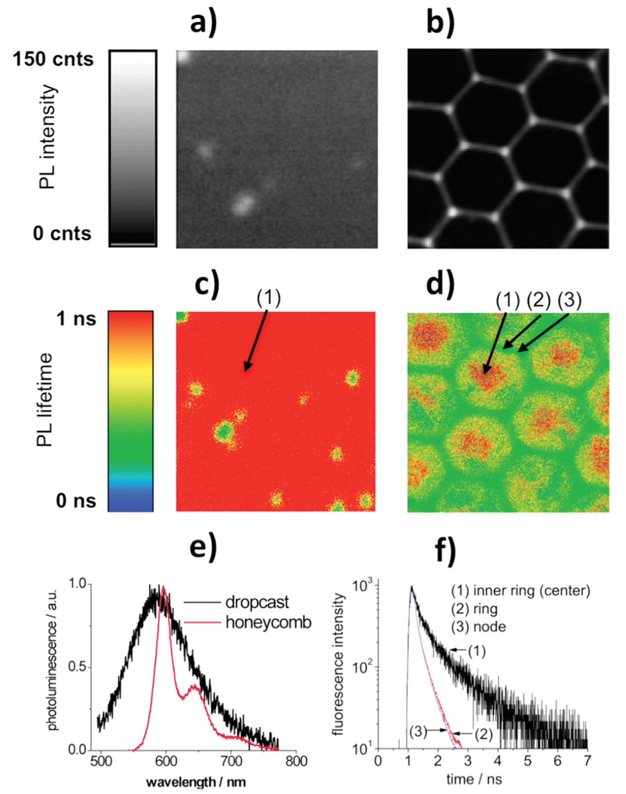

Figure 2. (a−d) confocal fluorescence microscopy (12 × 12 μm area) of dropcasted P1 and honeycomb PPV deposited from chlorobenzene. (a, b) Fluorescence intensity images of dropcast and honeycomb films, respectively; (c, d) FLIM images of dropcast and honeycomb films. (e) Diffraction-limited PL spectra of dropcast (black, homogeneous region) and honeycomb (red, node) films. (f) Diffraction-limited PL decays measured from P1-honeycomb at the inner ring (1), ring (2), and node (3). Regions 1−3 are indicated in panel d. The PL decay measured from region 1 in the dropcast film is identical to the decay of the P1-honeycomb measured at the inner ring (1) .

Table 1. Fluorescence Lifetimes and Contributions

sample	a_1	τ_1 (ns)	a_2	τ_2 (ns)	τ_{av} (ns)
P1-dropcasted	0.42	1.89	0.58	0.57	1.51
P1-honeycomb	0.13	0.83	0.87	0.23	0.43
P1/TM-C_{60} honeycomb	0.12	0.79	0.88	0.13	0.43
P1/EG-C_{60} honeycomb	0.72	0.37	0.28	0.08	0.24

It is noteworthy that the center of the hexagonal ring exhibits a longer PL lifetime (see Figure 2f, curve 1, average lifetime 1.5 ns) that is, similar to the homogenous region of the drop-casted film. This suggests that the center of the hexagonal ring of the honeycomb still contains an extremely thin layer of P1 polymer film. Thus, various parts of the hexagon

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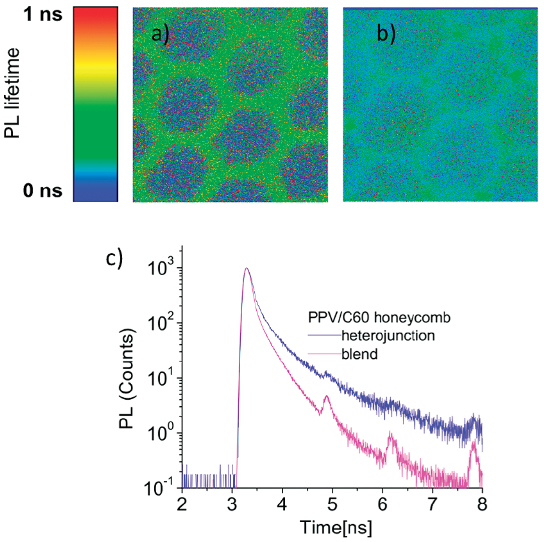

Figure 3. Confocal FLIM (12 × 12 μm) of (a) P1/TM-C_{60} honeycomb heterojunction and (b) P1/EG-C_{60} honeycomb blend. (c) Diffraction-limited PL decays measured from nodes for P1/fullerene honeycomb heterojunction (blue color) and blend (red color), respectively.

(center, frame and node) exhibit differing photophysical behaviors presumably due to a difference in polymer structures which are related to the time scale of solvent evaporation. The center of the hexagon is an extremely thin polymer layer which forms directly underneath the water-droplet. Rapid formation of this extremely thin film (similar to the dropcasted situation) is due to the fact that the polymer solution is quite thin as evaporation occurs. In contrast, the frame and nodes of the hexagon are situated in between water droplets, and the thickness of polymer solution at these regions is hundreds of nm, as suggested by AFM (see Figure S4 in the Supporting Information). Hence, formation of the fully evaporated film will be slower, with the possibility of forming more structured assemblies or aggregates of the polymer.

As an initial effort to demonstrate the implications of P1-honeycomb framework toward solar devices, we prepared P1/fullerene complexes either by immersion of the honeycomb into a methanol solution containing tris-(malonic acid) fullerene (TM-C_{60}, Figure 1a) or by starting BFT from a P1/emerald green fullerene (EG-C_{60}, Figure 1a) blend. For the P1/TM-C_{60} heterojunction honeycomb framework, dramatic quenching is observed mainly at the center of the hexagon rings (see Figure 3a), presumably due to the rather thin polymer layer in this region experiencing a good interfacial contact with TM-C_{60}. For the hexagonal rings, with a relatively thick polymer layer of these structures, quenching is apparently happening at the surface where good interfacial contact exists. Thus, the PL decay recorded from these regions exhibits only slightly quenched lifetimes compared to the undoped P1-honeycomb (see Figure 3c, blue colored curve, and Table 1). Structural characterization of P1/TM-C_{60} honeycomb indicates formation of particle aggregates of fullerene on top of the polymer honeycomb structure (see Figures S2c, S5b, S6c in the Supporting Information). For P1/EG-C_{60} honeycomb blend, the quenching by charge transfer is much more dramatic with nearly complete quenching at the frame and at nodes (Figure 3b). The PL decay recorded from hexagon nodes is severely quenched compared to that of the undoped honeycomb (Figures 2f and 3c) and it contains fast PL lifetimes associated with charge transfer (see Table 1). These results suggest efficient change transfer within the whole honeycomb when using the P1/EG-C_{60} blend. Structural characterization of P1/EG-C_{60} honeycomb blend (see Figures S2d, S5a, and S6b in the Supporting Information) indicates a well-defined structure, similar to that of pure P1-honeycomb, with no observable phase separation at the microscale, suggesting good miscibility between polymer and fullerene resulting in efficient charge transfer as demonstrated by FLIM (Figure 3b).

In conclusion, we have demonstrated preparation of highly regular P1 hexagonal honeycomb structures with 3−4 μm diameter and extended over large areas (1 mm^2) via the standard BFT method. The P1-honeycomb-patterns exhibit highly intense, red-shifted and vibronically structured photoluminescence compared to that of the drop-casted P1 films, likely reflecting regions of ordered close packing or enhanced $\pi-\pi$ stacking between polymer chains. Exciton dynamics on various portions of the hexagon indicate the existence of amorphous structure (hexagon centers) and ordered aggregates (hexagon frames). These structures result from differences in the thin-film formation process in each region. Finally, we demonstrated charge transfer through photoluminescence quenching upon complexation of P1-honeycomb with fullerene, either in heterojunction or in blend, the latter providing highly efficient charge transfer. Such behavior, combined with the high transparency of this framework, could be exploited in the future for the fabrication of photovoltaic windows, sensors, or organic solar cells.

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Supporting Information Available: P1-honeycomb preparation, complexation with fullerene, details on FLIM, stationary spectroscopy, AFM experiments, concentration-dependent honeycomb morphology (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.