Supplementary Information

Design, Fabrication and Charge Recombination Analysis of Interdigitated Heterojunction Nanomorphology on P3HT/PC$_{70}$BM Solar Cells

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SI-1. Fabrication conditions of NAAT

The samples of nanoporous anodic alumina template (NAATs) were fabricated in two-step anodization process. Table S1 summarizes the fabrication conditions.

<table>
<thead>
<tr>
<th>oxalic acid</th>
<th>V_{anod}^a (V)</th>
<th>t_{anod} (1^{st} step)^b (h)</th>
<th>t_{anod} (2^{nd} step) (s)</th>
<th>t_{pw}^c (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Template</td>
<td>H_2C_2O_4 (0.3 M)</td>
<td>40</td>
<td>24</td>
<td>60</td>
</tr>
</tbody>
</table>

\(^{a} V_{anod}\) is anodization voltage. \(^{b} t_{anod}\) is anodization time. \(^{c} t_{pw}\) is pore-widening time.

SI-2. Geometric characteristics of NAAT

The geometric characteristics of the resulting NAAT were got from ESEM image and Table S2 summarizes the values.

<table>
<thead>
<tr>
<th>Template of NAA (twenty samples)</th>
<th>(\phi_p)^a (nm)</th>
<th>(H_p)^b (nm)</th>
<th>(d_{int})^c (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 ± 4</td>
<td>80 ± 5</td>
<td>100 ± 4</td>
</tr>
</tbody>
</table>
\( \phi_p \) is pore diameter. \( H_p \) is pore height. \( d_{\text{int}} \) is interpore distance.

Figure S1 shows a physical sample of NAAT and the geometric characteristics.

**Figure S1** NAAT shows all its geometric characteristics.

**SI-3. NAAT ESEM images**

The characteristics of the resulting NAAT were got from ESEM image under different views.
Fig. S2 ESEM images of NAAT. (a) Top-view, (b) tilt-view and (c) cross section-view of NAAT. The geometrical characteristics were: \(\phi_{\text{pore}} = 60 \pm 4 \text{ nm}, \ H_{\text{pore}} = 80 \pm 5 \text{ nm} \) and \(d_{\text{inter}} = 100 \pm 4 \text{ nm}\).

SI-4. AFM images

Fig. S3 a, d and g show the topography images of P3HT–NP revealing a periodically structured top surface with an average nanopillar height of \(~80 \text{ nm}\) and interpillar distance \(~100 \text{ nm}\) as was seen in the ESEM images. P3HT:PC\(_{70}\)BM–BHJ has an average surface height of 13.39 nm and the P3HT–single layer has an average surface height of 23 nm, respectively. Fig. S3 b, e and h are shown the phase image and Fig. S3 c, f and I are shown the tilt view of the P3HT–NP, P3HT:PC\(_{70}\)BM–BHJ and P3HT–single layer, respectively.
Fig. S3 (a, b, c) AFM morphology, phase and tilt view images of the P3HT–NP layer after soft nanoimprinting by NAAT. (d, e, f) AFM morphology, phase and tilt view images of the P3HT:PC\textsubscript{70}BM–BHJ layer after spin coating deposition. (g, h, i) AFM morphology, phase and tilt view images of the P3HT–single layer after spin coating deposition. All the layers underwent thermal annealing at T = 130°C for t = 20 min.

SI-5. PL measurements

Fig. S4 shows the PL measurement for nanopillar samples and it was 16% greater in intensity than P3HT–flat film at 695 nm. On the other hand, after PL quenching the intensity of P3HT–
NP/PC$_{70}$BM–IHJN film was 94.8% lower than that of pure of P3HT–NP at 695 nm. For P3HT:PC$_{70}$BM–BHJ film and P3HT/PC$_{70}$BM–BL film the PL quenching was observed to be 85.3% and 92.7% lower than that of P3HT–flat film at 695 nm, respectively.

**Fig. S4** (Color on line) Photoluminescence spectres were obtained from P3HT nanopillars (red open circles) and P3HT– single film (green open squares). The same graph shows the PL spectrums from IHJN–[P3HT/PC$_{70}$BM] (red dashed line), BHJ–[P3HT:PC$_{70}$BM] (green continuous line) and BL–[P3HT/PC$_{70}$BM] (blue dotted line). The excitation wavelength was applied at 510 nm.

The best PL quenching of the three structures was for P3HT/PC$_{70}$BM–IHJN film. The total quenching of PL emission between the interfaces of polymer-fullerene might indicate that there is an efficient photoinduced and charge transfer at the interfaces of P3HT/PC$_{70}$BM materials.\(^1\),\(^2\) Therefore, on the P3HT–NP nanomorphology the interpillar distance between two nanopillar walls was 40 nm (maximum distance to D/A interface: 20 nm). This geometry may help the excitons to diffuse more easily at the polymer/fullerene composite interface (as it is well known that the exciton diffusion length is \(\sim 10\) nm in P3HT\(^3\),\(^4\)), which improves the performance parameters of the cells. By integrating the area below the PL spectra the electron injection yield from P3HT to PC$_{70}$BM can be estimated. In P3HT/PC$_{70}$BM–IHJN film, P3HT:PC$_{70}$BM–BHJ film and P3HT/PC$_{70}$BM–BL film these yields were 95%, 86% and 92%, respectively.
References