Characterization of PDPPBTT:PC$_{71}$BM bulk heterojunction nanostructures synthesized by a porous alumina template-assisted method

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Abstract. To enhance the charge transfer efficiency of bulk heterojunction materials, a nanostructure comprising blended PDPPBTT and PC.BM prepared via the porous alumina template-assisted method was proposed. Both materials were dissolved in chloroform in a 1:1 ratio at two different concentrations (5 and 10 mg mL$^{-1}$) and infiltrated into the nanopore template using a centrifuge method. The characterization results showed that one-dimensional nanostructures were successfully prepared. The high concentration solution resulted in nanostructures with large diameters but short lengths, which could absorb light effectively. Moreover, the high concentration solution exhibited low photoluminescence intensity, thus indicating efficient charge transfer from PDPPBTT to PC.BM.

Keywords: organic semiconductor, PDPPBTT, PC.BM, nanostructures, anodized aluminum oxide, hard template

1. Introduction
Organic semiconductors, which are economical and environmentally safe with unlimited availability, are increasingly being used in flexible optoelectronic device applications. They have high optical absorption coefficients. Hence, it is possible to fabricate thin-film devices via a low-cost approach [1]. For organic solar cell applications, a bulk heterojunction (BHJ) is the most preferred structure for active layers. BHJs comprise a mixture of electron donor and acceptor materials, which provides a large interfacial area for exciton dissociation into free electrons [2]. However, the efficiency of organic solar cells is still low compared to that of inorganic solar cells owing to inefficient charge transfer. To enhance the charge transfer efficiency, a nanostructured BHJ was proposed, which is expected to reduce the distance that the photogenerated free carriers have to travel to reach the respective electrodes; thus, the recombination can be greatly reduced [3–5].

In this study, a new low-band gap (1.38 eV) p-type semiconducting polymer, poly{2,2’-(2,5-bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydroxyphenyl[3,4-c]pyrrole-1,4diyl) dithieno[3,2-b]thiophene-5,5’-diyl-alt-thiophen-2,5-diyl} (PDPPBTT), was used in combination with a conventional n-type fullerene, [6,6]-phenyl C. butyric acid methyl ester (PC.BM), as the active layer materials in organic solar cells [6–9]. A simple and cost-effective hard template method based on nanoporous anodized aluminum oxide (AAO) was employed to fabricate the nanostructured active layer materials used in this experiment [10,11]. Although several methods exist to infiltrate organic materials into the nanopores of AAO templates, such as immersion and spin coating, in this experiment, a centrifuge method was selected owing to the strong centrifugal force that could push the materials into the nanopores to form better nanostructures [10,12,13]. The high density of the nanowires was proved to
Figure 1. Schematic of the position of the template inside a modified tube.

Figure 2. FESEM results of nanostructures produced at 3000 rpm with different solution concentrations: (a) 5 mg mL⁻¹ and (b) 10 mg mL⁻¹.

absorb at lower energies; this may enhance the optical properties by promoting the interchain interaction [13]. The dependences of the morphological, optical, and structural properties of blended PDPPBTT:PC₇₁BM materials on solution concentration were investigated in detail.

2. Materials and Methods
PDPPBTT (Mw > 30,000 GPC) and PC₇₁BM (Mw = 1030.93 g mol⁻¹) were purchased from Luminescence Technology Corp. and used without further purification. Porous alumina templates (Whatman Anodics, Sigma-Aldrich, St. Louis, USA) with pore diameters in the range of 20–200 nm and a thickness of 60 µm were used for synthesizing bulk heterojunction materials. Before the infiltration process, the template was cleaned by sonication in acetone, ethanol, and deionized water for 15 min each. Then, the template was rinsed with deionized water and dried completely at room temperature.

Mixture of PDPPBTT and PC₇₁BM with a ratio of 1:1 with two different concentrations, 5 mg mL⁻¹ (C5) and 10 mg mL⁻¹ (C10), were dissolved in chloroform and stirred for 24 h. Then, 100 µL of the solution was dropped onto the AAO template placed inside a modified tube (figure 1) in a centrifuge (Kubota B2420), as reported in a previous study [13]. The template surface was in the vertical position; hence, the centrifugal force horizontally infiltrated the solution into the pores of the template at 3000 rpm.

The UV–Visible absorption spectra of the PDPPBTT:PC₇₁BM nanostructure were recorded using Shimadzu UV-3101PC, and the Raman and photoluminescence (PL) spectra were recorded using Renishaw RE 04. For the morphological characterization, the template was removed first by dissolving alumina in 3 M sodium hydroxide (NaOH) solution for 24 h. The morphological characterization was analyzed by field emission scanning electron microscopy (FESEM; Hitachi SU-8030).

3. Results and discussion
The morphology of the PDPPBTT:PC₇₁BM nanostructure are shown in figure 2, which shows that one-dimensional nanostructures have been successfully prepared as a result of the pore shape in the template. The resulting structure also suggests that the solution could infiltrate the pores owing to a
Figure 3. (a) UV–Vis absorption and (b) photoluminescence spectra of PDPPBTT and PC.BM bulk heterojunction nanostructures prepared with two different solution concentrations.

Figure 4. Raman Spectra of PDPPBTT and PC.BM BHJ nanostructures prepared with two different solution concentrations.

A combination of centrifugal force and capillary force. However, figure 2 does not clearly show whether a nanorod or nanotube structure was formed, but in a previous study, this method resulted in a nanotube structure owing to the stronger intermolecular force between the liquid and the template surface compared with the cohesion force between the monomers in the solution [10]. The solution with a concentration of 10 mg mL⁻¹ produced nanotubes with an average diameter of 0.2 μm, while the solution with a concentration of 5 mg mL⁻¹ produced small nanotubes with an average diameter of 0.1 μm. In addition, the low concentration solution produced long nanotubes probably because the solution could penetrate deep into the pores owing to the low surface energy of the solution.

The UV–Vis absorption and PL spectra of PDPPBTT:PC.BM BHJ nanostructures are shown in figure 3. Two wide peaks centered at 420 and 720 nm can be observed in the UV–Visible absorption spectra (figure 3a), which originate from PDPPBTT absorption [6]. Materials with such a broad absorption spectrum are beneficial for solar cell applications owing to their ability to absorb the solar spectrum, of which 45% of the light is in the visible region [14]. High absorption intensity was obtained using the solution with a high concentration, which may be correlated with the morphology shown in figure 2, i.e., thick and short nanostructures can absorb light effectively. Moreover, there is a
Table 1. Raman peaks of PDPPBTT and PC.BM BHJ nanostructures prepared with two different solution concentrations.

| Peak | C5 (cm⁻¹) | C10 (cm⁻¹) | Assignments |
|------|-----------|-----------|-------------|
| V.   | 712       | 713       | symmetric C–S stretching |
| V.   | 1060      | 1055      | localized in-plane bending of thiophene C–H ip δ + stretching V₁₁₁ |
| V.   | 1192      | 1193      | C–H bending |
| V.   | 1230      | 1230      | (CH) torsion |
| V.   | 1326      | 1329      | (CH) twisting |
| V.   | 1370      | 1373      | in-plane bending of thiophene V₁₁₁ + C–H ip δ, Th V₁₁₁ |
| V.   | 1416      | 1413      | δ(CH) |
| V.   | 1517      | 1517      | Pentagonal pinch modes of the fullerenes |
| V.   | 1569      | 1569      | Anti-symmetric stretch modes of the fullerene |

slight red shift in the peak from 5 nm to 20 nm as the solution concentration is increased from 5 mg mL⁻¹ to 10 mg mL⁻¹; this indicates that there was more aggregation of chains in the high concentration sample than the low concentration sample. Polymer chains could align themselves and increase the conjugation length in the aggregated configuration, and the aligned polymer chains support more efficient electron excitation from π to π* and charge transfer between the DPP and bithiophene (BTT) units of the main chain [15]. The aggregation and chain alignment could enhance the optical properties by promoting the interchain and intrachain interactions [10].

The PL spectra of PDPPBTT:PC.BM BHJ nanostructures are shown in figure 3b. There are two peaks centered at 702 and 900 nm. The peaks may have resulted from the radiative recombination of two main excitation levels that correspond to the two absorbance peaks at short wavelengths. The peaks are also red-shifted from 709 nm to 715 nm and from 889 nm to 906 nm as the solution concentration is increased from 5 mg mL⁻¹ to 10 mg mL⁻¹. The low PL intensity for the high concentration sample indicates efficient charge transfer from PDPPBTT to PC.BM [9].

Figure 4 shows the Raman spectra of PDPPBTT:PC.BM BHJ nanostructures. Four peaks are observed at 1192, 1230, 1517, and 1589 cm⁻¹ that correspond to C–H bending for the first two peaks, the pentagonal pinch modes, and Raman active modes of the fullerene, respectively [16]. Furthermore, five peaks are observed at 712, 1060, 1326, 1370 and 1416 cm⁻¹ that originate from the PDPPBTT molecular motion [16,17]. Table 1 shows assignments of the Raman spectra for symmetric C–S stretching, a localized mode characterized by C–H in-plane bending together with C=C stretching at the thiophene ring, C–H bending of thiophene, C=C stretching in the DPP unit, and C=C stretching and C–C stretching of the BTT core and thiophene ring, respectively.

An upward shift of 10 mg/mL BHJ PDPPBTT:PC.BM for C–S stretching, C–H in-plane bending as well as C=C stretching in the thiophene unit together with C–H bending of the delocalized thiophene segment can be associated with better molecular arrangement seen at higher concentrations and also to a change in electron density from DPP to the acceptor moiety, so that, the C–C bond length of the material increases.

4. Conclusions

One-dimensional PDPPBTT:PC.BM bulk heterojunction nanostructures have been successfully fabricated using porous alumina templates and a centrifuge method. The high concentration solution (10 mg mL⁻¹) produced nanostructures with large diameters and short lengths owing to increased aggregation of the chains, resulting in high absorption intensity. Low photoluminescence intensity for the BHJ nanostructure was also obtained using the high concentration solution, which may be due to efficient charge transfer from PDPPBTT to PC.BM.

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