Formation of PCDTBT:PC\textsubscript{71}BM p–n junction composite nanotubes via a templating method†

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The use of a templating method to synthesize a p–n junction composite of poly[N-90-heptadecanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl 20,10,30 benzothiadiazole)] (PCDTBT):[6,6]-phenyl C\textsubscript{61} butyric acid methyl ester (PC\textsubscript{71}BM) is reported in this study. These materials have been studied due to their potential applications in organic electronic-based devices. Intimate contact between these materials can be realised via a facile fabrication using the template-assisted method. The formation of a p–n junction composite was elaborated in which its properties were compared to its bulk heterojunction counterpart. PCDTBT nanorods, nanotubes and nanoflowers were first produced followed by infiltration of PC\textsubscript{71}BM. A remarkable pattern at the first peak (carbazole) could be seen from the UV-vis spectra of the PCDTBT:PC\textsubscript{71}BM p–n junction composite nanotubes at a higher concentration of 15 mg ml\textsuperscript{-1}. However, the reverse condition was seen for its lower concentration of 5 mg ml\textsuperscript{-1}, which showed improvement in the second peak (DTBT) in the UV-vis spectra. The first peak of the 10 mg ml\textsuperscript{-1} solution concentration shows a wider peak compared to the 5 and 15 mg ml\textsuperscript{-1} concentrations with its second peak having fallen between these two concentrations. Unlike the PCDTBT:PC\textsubscript{71}BM bulk-heterojunction, which showed better quenching, PCDTBT:PC\textsubscript{71}BM composite nanotubes have shown a significant red-shift in their photoluminescence (PL) spectra. Despite having a significant red-shift, the PCDTBT:PC\textsubscript{71}BM junction composites displayed poor quenching properties.

Introduction

Conjugated polymers have been broadly used in various technologies such as organic photovoltaics (OPVs), organic light emitting diodes (OLED) and sensors due to their favourable properties.\textsuperscript{1–4} These favourable properties are highly reliant on the preparation methods and the resulting nanostructures.\textsuperscript{5,6} Nanostructures of conjugated polymers such as nanorods, nanowires, nanoflowers and nanotubes\textsuperscript{7–9} are some of the outstanding approaches in the development of versatile fabrications. The physical and chemical properties of polymers such as the degree of polymerization, molar mass distribution, crystallinity and intermolecular properties can be altered by varying the fabrication technique.

Poly[N-90-heptadecanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl 20,10,30 benzothiadiazole)] (PCDTBT) is the most promising p-type conjugated polymer that possesses outstanding structural, optical and electronic properties.\textsuperscript{1,4,6–9,10} Recently, PCDTBT has been extensively used as an active layer by either incorporating it with n-type materials in a bulk heterojunction system or as a single nanostructured material.\textsuperscript{6,9–11}

The synthesis of the polymer composite at the nanoscale has received much attention. Polymer composites that are composed of both p- and n-type materials have a potential to enhance the charge carrier separation, charge carrier transfer and light absorption due to the formation of a p–n junction.\textsuperscript{1,4,7–11}

The template-assisted method is one of the most considered methods for fabricating the innumerable polymer composite architectures due to its mass production capabilities with minimal investment of cost and time.\textsuperscript{6,12–14} The most common techniques used in the templating method are immersion (template wetting) and spin coating.\textsuperscript{6,7,15,16} The spin coating technique has been widely used in fabricating the bulk heterojunction based devices such as OPVs, OLED and sensors by blending the p- and n-type materials.\textsuperscript{4,11,17–19} By blending these materials, interpenetrating structures are later produced, thus creating the bulk heterojunction system. Researchers have alternatively incorporated the conjugated polymer (p-type) and fullerenes (n-type), in order to provide charge transfer within the blends.\textsuperscript{4,10,21} Practically, fullerenes such as [6,6]-phenyl C\textsubscript{61} butyric acid methyl ester (PC\textsubscript{61}BM) and [6,6]-phenyl C\textsubscript{71}butyric acid methyl ester (PC\textsubscript{71}BM) have an energetic deep lying LUMO which bestows the molecule with a high electron affinity relative...
to the various potential organic donors thus making it an ideal n-type material.\textsuperscript{22,23}

To the authors’ best knowledge, studies involving one dimensional nanostructures of the PCDTBT:fullerene junction composite have not been reported. The template-assisted method is useful in producing a heterostructured composite via a simple layer by layer approach (two different materials incorporated together at a different time) such as composite nanotubes and nanorods.\textsuperscript{3,5,7,15} Since the charge separation of excitons is taking place at the interface between the p- and n-type, an intimate contact of both materials is required for the efficient splitting of the photogenerated excitons. To fulfil the vigorous charge carrier splitting, large interfacial areas are greatly needed, which in turn yields higher charge generation rates. Intimate contact at the nanoscale could be realized from the formation of the p-n junction composite nanostructure. On the other hand, the bulk heterojunction has been limited by its charge percolation within the intermixed phases. In this study, PCDTBT:PC\textsubscript{71}BM junction composite nanostructures and bulk charge percolation within the intermixed phases. In this study, the other hand, the bulk heterojunction has been limited by its formation of the p

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emission scanning electron microscopy (HRTEM) (Hitachi HT7700, Japan), UV-vis spectroscopy (Lambda 750, Perkin Elmer, Waltham, USA), photoluminescence spectroscopy (Renishaw, Gloucestershire, UK) and Raman spectroscopy.

**Results and discussion**

Fig. 1a–c show the FESEM images of PCDTBT nanorods, nanotubes and nanoflowers that are produced from a 5, 10 and 15 mg ml\textsuperscript{-1} solution concentration, respectively. These nanostructures are obtained after the dissolution of the template prior to the infiltration of the PC\textsubscript{71}BM solution. Fig. 2 shows the FESEM images of PCDTBT:PC\textsubscript{71}BM composites synthesized from a 5 mg ml\textsuperscript{-1} solution concentration. Obviously, with a lower spin coating rate of 1000 rpm, most of the PCDTBT nanorods are intact, however, with a lower p–n junction composite formation (Fig. 2a and b). Some of the nanorods are broken at the tips and collapsed into non-aligned structures. The base appears to be branched due to the existing branched structures of the commercial porous alumina template. Both nanorods and nanotubes are visible, however, at a spin coating rate of 1000 rpm the structures are dominated by nanotubes. Formation of nanorods is assumed to originate from PCDTBT itself. This assumption is due to the observation of PCDTBT nanorods that are confined inside the template before the dissolution process. Since the low spin coating rate of the PC\textsubscript{71}BM solution is applied, one could expect that high dissolution of PC\textsubscript{71}BM on the PCDTBT nanorods may have been occurred due to the usage of a similar solvent (chloroform). Consistency of dissolution can be observed from the existence of diffuse reflection peaks of PCDTBT and PC\textsubscript{71}BM in the UV–vis absorbance spectra.

**Experimental**

PCDTBT and PC\textsubscript{71}BM were purchased from Luminescence Technology Corp (Taiwan, ROC) and Sigma Aldrich (St. Louis, USA), respectively, and used without further purification. PCDTBT and PC\textsubscript{71}BM were separately dissolved in chloroform for a solution concentration of 5 mg ml\textsuperscript{-1} (sample A), 10 mg ml\textsuperscript{-1} (sample B) and 15 mg ml\textsuperscript{-1} (sample C). For the bulk heterojunction samples, a blend mixture of PCDTBT: PC\textsubscript{71}BM with a ratio of 1:1 was also prepared for 5, 10 and 15 mg ml\textsuperscript{-1}. Porous alumina templates (Whatman Anodisc, Sigma-Aldrich, St. Louis, USA) and glass substrates were used for synthesizing the p–n junction composite nanostructures and bulk heterojunctions, respectively. The glass substrate (sail Brand, China) and porous alumina template were both cleaned by sonicating in acetone, ethanol and deionized water for 15 min prior to oven drying and nitrogen blowing.

PCDTBT:PC\textsubscript{71}BM junction composite nanotubes were prepared using the spin coating technique. 5, 10 and 15 mg ml\textsuperscript{-1} of the PCDTBT solution were first spin coated onto the alumina template followed by spin coating of 5, 10 and 15 mg ml\textsuperscript{-1} of the PC\textsubscript{71}BM solution. Three different spinning rates of 1000 (sample 1), 2000 (sample 2) and 3000 rpm (sample 3) were applied throughout the coating. Afterwards, these samples were dried at room temperature prior to the dissolution process. Template dissolution was conducted for 12 h by immersing the template in 4 M sodium hydroxide (NaOH). Meanwhile, the bulk heterojunction samples were prepared by blending PCDTBT and PC\textsubscript{71}BM before the spin coating took place. Characterisations of their morphological, structural and optical properties were carried out by field emission scanning electron microscopy (FESEM) (JSM 7600-F, JEOL Ltd., Tokyo, Japan), high resolution transmission electron microscopy (HRTEM) (Hitachi HT7700, Japan), UV-vis spectroscopy (Lambda 750, Perkin Elmer, Waltham, USA), photoluminescence spectroscopy (Renishaw, Gloucestershire, UK) and Raman spectroscopy.

![FESEM images of the PCDTBT nanorods (a), nanotubes (b) and nanoflowers (c).](image)

Fig. 1
of the composite nanorods at the branched bases. The spin coating rate could lead to a fast or slow solvent evaporation rate. At a spin coating rate of 1000 and 2000 rpm, the solvent experiences a slow evaporation rate which could help to improve the order of the polymer chain hence providing an improvement in the morphology of the PCDTBT:PC$_{71}$BM p–n junction composite nanotubes. However, a spin coating rate of 3000 rpm has a fast solvent evaporation rate which could lead to a low degree of morphology. These explanations are supported by the FESEM images shown in Fig. 2c–f. At a spin coating rate of 2000 rpm (Fig. 2c and d), uneven penetration of the PC$_{71}$BM solution has occurred and the formation of the p–n junction composite is observed. There are two different regions, bright and dark, which correspond to PCDTBT and PC$_{71}$BM, respectively. A higher spin coating rate of 3000 rpm has led to the formation of thin-walled nanotubes that easily split and collapse during the dissolution process (shown by the red arrows in Fig. 2e). This phenomenon could be due to low availability of the PCDTBT solution at the beginning of the flow. It is believed that some of the solution had been splashed away during the infiltration process due to the high spin coating rate. Furthermore, the low viscosity of the 5 mg ml$^{-1}$ solution also increases the possibility of splashing in a large amount. As shown in Fig. 2f, the flat tip of the remaining PCDTBT nanorods is observed although after the incorporation of PC$_{71}$BM, which further confirms the decrease in availability of the PC$_{71}$BM solution during the higher spin coating rate of 3000 rpm.

Fig. 3a–f show the FESEM images of the PCDTBT:PC$_{71}$BM p–n junction composite with a 10 mg ml$^{-1}$ solution concentration that was fabricated at three different spin coating rates of 1000, 2000 and 3000 rpm. As can be seen from the images, the higher spinning rate of 3000 rpm produced shorter nanotubes compared to the slower spinning rate of 1000 and 2000 rpm. The distance from the top to the Y-branched structure indicates the improved infiltration achieved by the lower spinning rate. Infiltration has occurred throughout the channel which led to longer nanotubes. As mentioned earlier, a sufficient polymer supply that does not splash away at the beginning of spinning could contribute to the longer (higher aspect ratio) composite nanotubes which usually occur at a lower spinning rate. This reason could also contribute to the production of denser nanotubes (1000 rpm) which can be seen from the bigger island caused by fewer collapsing nanotubes (due to the little space created between the nanotubes). Fig. 3a, c and e (inset) show the collapsed and agglomerated nanotubes at the tips due to the thin wall at the top (end of the flow).

Fig. 4a–f show the FESEM images of the PCDTBT:PC$_{71}$BM p–n junction composite with a 15 mg ml$^{-1}$ solution concentration that was fabricated at three different spin coating rates of 1000, 2000 and 3000 rpm. The p–n junction composite nanotubes that have been synthesized at a higher solution concentration exhibit longer and less broken (stable) structures compared to the structures that were synthesized at a lower solution concentration. As reported elsewhere, a higher solution concentration with higher viscosity would give a better infiltration and aspect ratio. A viscous solution could prevent the
polymer from splashing in a large amount during spinning unlike the less viscous solution which tends to easily splash away. Therefore, a more viscous solution will provide a huge availability of the polymer solution to undergo the infiltration process. In addition, a viscous polymer solution will give a thicker PCDTBT:PC71BM composite nanotube wall which could lead to stable and less broken nanotubes. The distance of the travelling solution throughout the porous nanochannel (template) will indicate the thickness of the nanotube walls. As the solution travels deeper into the nanochannel, the nanotube walls will tend to get thinner. Fig. 4a shows the agglomeration and joining tips of the composites due to the extremely thinner walls which do not break but tend to collapse with each other during the dissolution process. On the other hand, Fig. 4c and e show the formation of meniscus tips with less visible agglomeration, which may be due to the high spin coating rate. Theoretically, a solution has a tendency to splash away in a large amount of solution, which allows only a small presence of the polymer solution for infiltration. This phenomenon is supported by Fig. 4b, d and f in which broken nanotubes are likely to form with the spin coating rate of 1000 rpm. The higher spin coating rate produced slightly thicker walls than the former and has contributed to more stable structures by preventing the agglomeration of tips (despite being broken at the meniscus). Most of the nanotubes are broken at the tip meniscus due to the formation of a thinner wall at the end of the flow (tip) compared to the thicker wall at the base which acts as the starting point of the flowing fluid. A fast evaporation rate and decreased amount of polymer solutions at the tips during nanotube growth could also lead to the thinning of the walls.

HRTEM images of the individual PCDTBT:PC71BM p–n junction composite nanotubes with 5, 10 and 15 mg ml\(^{-1}\) solution concentrations are shown in Fig. 5a–c, d and e, respectively. The HRTEM image of 5 mg ml\(^{-1}\) PCDTBT:PC71BM composite nanotubes (Fig. 5a) is well correlated with their FESEM images shown in Fig. 2d with the appearance of dissolution by the PC71BM solution. The HRTEM image in Fig. 5b confirms the presence of PCDTBT nanorods which originated from the confined PCDTBT that was exempted from dissolution by PC71BM. The HRTEM image of the 10 mg ml\(^{-1}\) based p–n junction composite nanotubes shows some uneven coating of PC71BM on the surface of the PCDTBT layer. 15 mg ml\(^{-1}\) based p–n junction composite nanotubes garnered a better stability of definite nanotubes (Fig. 5c and d). The outer (PCDTBT) and inner layer (PC71BM) of the composite nanotubes show the consecutive formation of a p–n junction due to the incorporation of spin-coated PC71BM. Two different regions, bright and dark, can be seen in the PCDTBT:PC71BM composite nanotubes of all solution concentrations which represent PCDTBT and PC71BM, respectively.

Fig. 6a–c illustrate the formation of 5, 10 and 15 mg ml\(^{-1}\) of the PCDTBT:PC71BM p–n junction composite and the structure transition due to the spin-coating of PC71BM onto the confined PCDTBT nanorods, respectively, based on the general observations made from FESEM and HRTEM images. Due to the usage...
of a similar solvent (chloroform) for both PCDTBT and PC_{71}BM, the existing formation of the confined p-type has been distorted by the n-type solution. Although, the different spin coating rates of 1000, 2000 and 3000 rpm are applied for only 30 s during the deposition of the n-type, it is enough to just dissolve a middle portion of the confined PCDTBT to become a porous structure. Consequently, PC_{71}BM will be able to infiltrate into the p-type and forms the PCDTBT:PC_{71}BM junction composite nanotubes. The faster evaporation rate and stronger adhesive forces also promote the formation of the PCDTBT:PC_{71}BM junction composite nanotubes and inhibit the complete infiltration of the polymer solution. Fig. 6a(i–vi) shows an illustration of the uneven distribution of PC_{71}BM after dissolution of the template which is likely to occur with the lower solution concentration of 5 mg ml^{-1}. The spin coating techniques used to deposit both p- and n-types and a less viscous solution (5 mg ml^{-1}) could be the ultimate reasons for the formation of a thinner wall. The immersion technique followed by the spin coating technique of the same concentration of 5 mg ml^{-1} has been reported to exhibit more stable nanotubes. The sufficient time provided by the immersion technique has enhanced the wetting and coating thickness of the polymer solution on the template wall. Some of the PCDTBT nanorods remain as they were although the incorporation of PC_{71}BM has occurred. Fig. 6b(i–v) elucidates the formation of 10 mg ml^{-1} of the PCDTBT:PC_{71}BM p-n junction composite and the coating mechanism of PC_{71}BM on the inner surface of the PCDTBT nanotube. Instead of a solid nanostructure (nanorods and nanoflowers), a 10 mg ml^{-1} composite has produced a hollow PCDTBT nanostructure (nanotubes). The different spinning rates of 1000, 2000 and 3000 rpm of the PC_{71}BM solution will help to coat the PCDTBT nanotube inner layer in a spiral motion and led to the uneven coating as shown in the HRTEM image of Fig. 5c. A solution concentration of 15 mg ml^{-1} has improved the morphology of the PCDTBT:PC_{71}BM composite nanotubes (Fig. 6c(i–vi)). Incorporation of PC_{71}BM into the PCDTBT nanorods that were confined inside the template channel has caused some changes in the physical properties of the final formation of PCDTBT:PC_{71}BM. The thinning of the nanotube wall as the solution flows through the channel occurred for all concentrations of 5, 10 and 15 mg ml^{-1}.

Fig. 7 shows the UV-vis spectra of the PC_{71}BM thin film, PCDTBT thin film and the PCDTBT:PC_{71}BM bulk heterojunction with different solution concentrations and spin coating rates. The PCDTBT thin film shows significant peak absorption between 350–650 nm in the UV and visible region which represents the carbazole (Cz) donor and dithienylbenzothiadiazole (DTBT) acceptor, respectively. The UV-vis spectrum of the PCDTBT thin film portrayed a broad valley between 400–500 nm while the UV-vis spectrum of the PC_{71}BM composite nanotubes of 5 mg ml^{-1} (a), PCDTBT:PC_{71}BM composite nanotubes of 10 mg ml^{-1} (b), and PCDTBT:PC_{71}BM composite nanotubes of 15 mg ml^{-1} (c).
thin film shows its main peak absorption between 450–500 nm. It can be observed that, the main peak of DTBT located at 580 nm decreases in intensity, while the middle valley (500 nm) showed an increased intensity after the incorporation of PCDTBT and PC71BM for both concentrations (5 and 15 mg ml⁻¹) which represents the mixed state of the two parent materials. By incorporating these two materials, a broader absorption peak in the visible region can be recognized. The solution concentration has played a vital role in eliciting the significant difference in terms of the optical properties (wider absorption band at a longer wavelength), in which 5 mg ml⁻¹ of the bulk heterojunction film shows a red-shift and wider absorption compared to its 15 mg ml⁻¹ counterpart. The solution concentration and polymer–fullerene ratio have evoked a strong influence on the aggregation behaviour of the blends which are related to the red-shift (absorption edge transition) of the optical absorption spectra.

Fig. 8a shows the absorption spectra of the PCDTBT nanoflowers and PCDTBT nanorods which are well correlated with a previous report.⁶ The UV-vis absorption spectrum of the PCDTBT nanoflowers shows a red-shift and wider absorption at its second peak whereas the UV-vis absorption spectrum of the PCDTBT nanorods shows a red-shift at its first peak. The absorption edge of the PCDTBT nanotubes (10 mg ml⁻¹) is consistent with PCDTBT nanorods (5 mg ml⁻¹) and nanoflowers (15 mg ml⁻¹) which falls between these two concentrations. The optical properties between 5 mg ml⁻¹ of the PCDTBT:PC71BM composite nanotubes and their bulk heterojunction films are compared (Fig. 8b). PCDTBT:PC71BM bulk heterojunction films exhibited a prominent intensity and red-shift at its second peak. However, a wider peak absorption is dominant in PCDTBT:PC71BM composite nanotubes at all spin coating rates. A wider peak absorption also can be seen for the 10 mg ml⁻¹ composite nanotubes as compared to their bulk heterojunctions (Fig. 8c). Overall, the higher solution concentration of the PCDTBT:PC71BM composite nanotubes has shown better optical absorption across all spectra than that of their bulk heterojunction film counterparts (Fig. 8d). A remarkable pattern for peak absorption of the bulk heterojunctions at all three concentrations (5, 10 and 15 mg ml⁻¹) can be clearly seen from the UV-vis spectra which show a prominent peak intensity and peak narrowing beyond their composite nanotubes. However, the widening of the peak absorption is dominated by the composite nanotubes of all solution concentrations. The PCDTBT:PC71BM composite nanotubes of 15 mg ml⁻¹ have a dominant red-shift at the first peak which corresponds to the Cz donor (Fig. 8e). Although, a red-shift at the second peak has not occurred, a wider absorption of the second peak is clearly seen. PCDTBT:PC71BM composite nanotubes of 5 mg ml⁻¹ show a significant absorption edge transition to a longer wavelength (red shift) in the peak which corresponds to the DTBT acceptor. If a comparison was to be made in terms of the red-shift in the second peak between the composite nanotubes and bulk heterojunction films, the latter seem to exhibit a promising shift.

PC71BM has acted as a defect site which disrupts the ordered packing of the PCDTBT chain during the solvent
removal process. Disruption is increased with the increasing amount of PC_{71}BM which then decreases the conjugation length or blue-shift. Changes in the dominancy of peak absorption are realised by changing the solution concentration of the composite nanotubes. A low concentration of the polymer–fullerene system has a wider absorption range at a longer wavelength due to the suppression of PC_{71}BM aggregate growth at a low concentration, which led to the optimisation and stable phase separation between the interfaces. The solution concentration of the polymer imposed a strong influence on the aggregation behaviour and was significantly related to the red-shift of the UV-vis absorption peak. Within the polymer–fullerene system, the probability of the polymer solution to entangle is reduced in a diluted solution, which promotes the formation of aggregates. A diluted solution has a higher degree of freedom (to flow) which enables aggregation, while the probability of the polymer solution to entangle increases in a higher concentration of solution which precludes the formation of aggregates.

Fig. 9a shows PL spectra of the PCDTBT nanorods, PCDTBT nanotubes and PCDTBT nanoflowers. Little quenching is seen apart from a shift in the peak for PCDTBT nanotubes and PCDTBT nanoflowers. Significant quenching can be seen for PCDTBT nanotubes compared to PCDTBT nanorods and nanoflowers. PCDTBT nanoflowers (peak at 701 nm) have undergone a slight red-shift whereas PCDTBT nanorods (peak at 692 nm) have become slightly quenched. Between these three PCDTBT nanostructures, PCDTBT nanoflowers show the most significant shifting to lower energy. As shown in Fig. 9b–d, PL spectra of the composites exhibited a prominent difference compared to the single material. PCDTBT:PC_{71}BM composite nanotubes showed favourable luminescence properties for quenching and shifting compared to the single material of PCDTBT nanorods, PCDTBT nanotubes and PCDTBT nanoflowers. PCDTBT:PC_{71}BM composite nanotubes of 5 mg ml^{-1} that were coated at 1000, 2000 and 3000 rpm exhibited a maximum PL peak at 714, 715 and 712 nm, respectively. Meanwhile, PCDTBT:PC_{71}BM composite nanotubes of 10 mg ml^{-1} that were spin coated at 1000, 2000 and 3000 rpm exhibited a maximum PL peak at 720, 721 and 719 nm, respectively. PL peaks at 722, 718 and 721 nm were seen for PCDTBT:PC_{71}BM composite nanotubes of 15 mg ml^{-1} that were spin coated at 1000, 2000 and 3000 rpm, respectively. Quenching of the PL spectra of the PCDTBT:PC_{71}BM composite nanotubes is related to the photo-induced charge separation between the electron donor (PCDTBT) and electron acceptor (PC_{71}BM) molecules. The presence of PC_{71}BM (guest) will facilitate energy flow and allows for inter and intra-chain energy transfer to be efficiently separated. Additionally, the thin wall of the nanotubes offers a short distance to facilitate ion transport while hollow nanotubes permit counter ions to readily penetrate into the composite material. However, bulk heterojunction films of all concentrations (5, 10 and 15 mg ml^{-1}) are more significantly quenched compared with the composite nanotubes (Fig. 9e). Higher emission peaks would suggest radiative recombination and sub-optimal nanostructures within the composite nanotube system. Strong surface tension generated at the interface...
between the nanotubes and the solvent during the solvent evaporation and dissolution processes could be one of the greatest contributors to the sub-optimal nanostructures. On the other hand, the red-shift of the PL spectra at 714, 720 and 722 nm in the composite nanotube system is due to the increase in the Stokes shift which also implies that the polymer chain became more rigid. The increase in rigidity is associated well with a better alignment state of the polymer chains in the porous alumina template. The extra longer chains allowed for the higher diffusion rate of PC71BM into PCDTBT due to the increase of interspacing between backbones, which resulted in a larger scale phase separation between compounds. This could be the main reason for the red-shift of the composite nanotubes but less quenching when compared to their bulk heterojunction films.

Fig. 10a–d show the Raman spectra of the 5 mg ml\(^{-1}\) PCDTBT:PC71BM composite nanotubes and their bulk heterojunction films, 10 mg ml\(^{-1}\) PCDTBT:PC71BM composite nanotubes and their bulk heterojunction films, 15 mg ml\(^{-1}\) PCDTBT:PC71BM composite nanotubes and their bulk heterojunction films and PCDTBT and PCBM thin films. Comparison of the Raman spectra between PCDTBT thin films and PC71BM thin films have shown that there are peaks that exist for PC71BM but not for PCDTBT which are assigned to C–H bending at 1191 and 1231 cm\(^{-1}\), pentagonal pinch modes of the fullerene at 1569 cm\(^{-1}\) and Raman active modes of the fullerene at 1568 cm\(^{-1}\). There are some peaks that arise due to PCDTBT molecular motion located at 843, 871, 1065, 1271, 1349, 1373, 1445, 1541, and 1622 cm\(^{-1}\) which are well correlated with previous reports. These peaks are assigned to symmetric C–S stretching, asymmetric C–S stretching, a localized mode characterized by C–H in-plane bending together with C=C stretching at the thiophene ring, C–H in-plane bending and C=C stretch bending of the benzothiadiazole delocalized mode as well as C–H in-plane bending with C=C stretching for both the carbazole and thiophene unit, delocalized motion involving the benzothiadiazole, thiophene, and carbazole unit for 1349 and 1373 cm\(^{-1}\), localized motion involving carbazole, thiophene and benzothiadiazole, localized motion involving the carbazole unit only, localized motion involving the benzothiadiazole unit only and localized motion involving the carbazole unit which is related to the C–H in-plane bending together with C=C stretching.

Assignments and changes in the wavenumber band between PCDTBT:PC71BM composite nanotubes, bulk heterojunction thin films and PCDTBT and PC71BM thin films are tabulated in Tables 1–3, respectively. 15 mg ml\(^{-1}\) of the PCDTBT thin film shows a slightly upward shift of several peaks that represents symmetric and asymmetric C–S stretching, localized motion involving the carbazole unit (C–H bending, C=C stretching, C–N stretching and C–H in-plane bending) and the thiophene unit (C–H bending and C=C stretching) and symmetric C=C and C–H in-plane bending of the carbazole part which can be related to the change in the bond order of the PCDTBT chain backbone. Other peaks at 1065, 1271, 1349 and 1373 cm\(^{-1}\) remain unchanged for both the 5 and 15 mg ml\(^{-1}\) PCDTBT thin film that are assigned to C–H in-plane bending + C=C stretching.
A1 A2 A3 B1 B2 B3 C1 C2 C3 Assignments
842 842 841 843 843 844 841 842 842 Sym C=S stretch
871 871 871 875 876 874 872 870 873 Asym C=S stretch
1062 1062 1065 1069 1067 1064 1062 1063 1066 L: Th CH \( \text{ip} \) \( \delta + V_{C=C} \)
1189 — — — — 1189 — 1190 C-H \( \delta \)
1228 — — — — 1228 — 1229 C-H \( \delta \)
1270 1270 1271 1270 1271 1271 1270 1270 1271 D: BT \( \delta + V_{C=C} + C-H \) \( \delta \), Cz + Th CH \( \text{ip} \) \( \delta + V_{C=C} \)
1346 1347 1347 1350 1350 1349 1346 1347 1347 D: BT + Th \( \text{CH} \) \( \delta \), Cz + BT \( V_{C=N} \)
1347 1347 1372 1375 1375 1375 1371 1371 1373 BT + Th + Cz \( V_{C=C} + C-H \) \( \text{in-plane} \) \( \delta \), Cz \( V_{C=N} \)
1444 1444 1444 1447 1446 1448 1444 1444 1445 L: Cz Th \( V_{C=C} + CH \) \( \text{ip} \) \( \delta \), Cz \( V_{C=N} \)
1540 1540 1540 1540 1540 1541 1540 1538 1541 L: BT + Th sym \( V_{C=C} \), CH \( \text{ip} \) \( \delta \)
1566 1566 1565 1567 1568 1567 1566 1564 1567 Antisymmetric stretch modes of the fullerene
1619 1619 1620 1624 1624 1620 1621 1619 1621 L: Cz \( V_{C=C} + CH \) \( \text{ip} \) \( \delta \)

* Sym, symmetric; asym, asymmetric; L, localized; Th, thiophene; ip, in-plane; \( V_{a-b} \), stretch of the a-b bond; \( \delta \), bend; D, delocalized; BT, benzothiadiazole; Cz, carbazole.

### Table 2 Raman peak position of the PCDTBT:PC71BM bulk heterojunction thin films of 5, 10 and 15 mg ml\(^{-1}\)

<table>
<thead>
<tr>
<th>BHJ</th>
<th>10 mg ml(^{-1})</th>
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<th>Assignments</th>
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<td>841</td>
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<td>842</td>
<td>Sym C-S stretch</td>
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<td>L: Th CH ( \text{ip} ) ( \delta + V_{C=C} )</td>
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<td>1270</td>
<td>1271</td>
<td>D: BT ( \delta + V_{C=C} + C-H ) ( \delta ), Cz + Th CH ( \text{ip} ) ( \delta + V_{C=C} )</td>
</tr>
<tr>
<td>1348</td>
<td>1349</td>
<td>1349</td>
<td>D: BT + Th CH ( \delta ), Cz + BT ( V_{C=C} )</td>
</tr>
<tr>
<td>1373</td>
<td>1374</td>
<td>1373</td>
<td>BT + Th + Cz ( V_{C=C} + C-H ) ( \text{in-plane} ) ( \delta ), Cz ( V_{C=N} )</td>
</tr>
<tr>
<td>1445</td>
<td>1447</td>
<td>1446</td>
<td>L: Cz Th ( V_{C=C} + CH ) ( \text{ip} ) ( \delta ), Cz ( V_{C=N} )</td>
</tr>
<tr>
<td>1539</td>
<td>1540</td>
<td>1541</td>
<td>L: BT + Th sym ( V_{C=C} ), CH ( \text{ip} ) ( \delta )</td>
</tr>
<tr>
<td>1621</td>
<td>1622</td>
<td>1621</td>
<td>Antisymmetric stretch modes of the fullerene</td>
</tr>
</tbody>
</table>

* Sym, symmetric; asym, asymmetric; L, localized; Th, thiophene; ip, in-plane; \( V_{a-b} \), stretch of the a-b bond; \( \delta \), bend; D, delocalized; BT, benzothiadiazole; Cz, carbazole.
C–N stretching (1373 cm\(^{-1}\)), C=C stretching and C–H in-plane bending of the delocalized benzothiadiazole, carbazole and thiophene unit (1261 and 1271 cm\(^{-1}\)).

A downward Raman shift shows that the incorporation of PC\(_71\)BM has an impact on the molecular structure reorganization of PCDTBT. A Raman peak at 1191 cm\(^{-1}\), which is assigned to C–H bending (PC\(_71\)BM thin film), only appeared for the 15 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes with bands at 1189 and 1190 cm\(^{-1}\). A Raman shift at 1231 cm\(^{-1}\), which indicates C–H bending in PC\(_71\)BM molecular structures, only appeared for the 15 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes and diminished in the 5 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes. C–H bending has undergone a downward shift of ~3 cm\(^{-1}\) and 2 cm\(^{-1}\) to 1228 and 1229 cm\(^{-1}\) for the 15 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes. A Raman shift at 1470 cm\(^{-1}\) for higher concentrations is seen for pentagonal pinch modes of the fullerenes which also occurred in the 15 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes with a downward shift of 1467 and 1468 cm\(^{-1}\). The Raman active modes of fullerenes that occurred at 1568 cm\(^{-1}\) (ref. 33) are similar for both concentrations. A downward shift of the Raman peaks for almost all PCDTBT peaks after the incorporation of PC\(_71\)BM is indicative of the strong influence of PC\(_71\)BM on the molecular level for PCDTBT and vice versa. A significant downward shift of all PC\(_71\)BM peaks after incorporation with PCDTBT shows the impact of PCDTBT on the molecular level of PC\(_71\)BM. Peaks that represent PC\(_71\)BM were only seen at the higher concentration 15 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes except for the Raman active mode of fullerene which was seen for all concentrations. Peaks that were assigned to different molecular alterations have arisen due to the formation of the PCDTBT:PC\(_71\)BM composite nanotubes.

Delocalized benzothiadiazole + thiophene C–H bending and carbazole + benzothiadiazole C=C stretching lead to a significant downward shift of ~2 cm\(^{-1}\) for the PCDTBT:PC\(_71\)BM composite nanotubes and not for their bulk heterojunction films. The same goes for C=C stretching + C–H in-plane bending of delocalized benzothiadiazole + thiophene + carbazole and carbazole C–N stretching in which the shift only exists for the composite nanotubes. 15 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes have experienced a significant downward shift of ~3 cm\(^{-1}\) (1619 cm\(^{-1}\)) and 2 cm\(^{-1}\) (1621 cm\(^{-1}\)), ~2 cm\(^{-1}\) (1620 cm\(^{-1}\)) for 10 mg ml\(^{-1}\) composite nanotubes, while 5 mg ml\(^{-1}\) PCDTBT:PC\(_71\)BM composite nanotubes shift to 1619 cm\(^{-1}\) and 1620 cm\(^{-1}\) from 1622 cm\(^{-1}\).

### Conclusions

In this work, PCDTBT:PC\(_71\)BM p–n junction composite nanotubes have been synthesized via a templating method of a spin coating technique using a simple layer by layer approach. The optimal concentration of single and composites materials has been revealed. With comparison to 3000 rpm, a spin coating rate of 1000 and 2000 rpm produces a more stable composite nanotube for all concentrations of 5, 10 and 15 mg ml\(^{-1}\). The stability of the composite nanotube increases as the concentration increases. A higher concentration of 15 mg ml\(^{-1}\) produces more definite and fewer broken composite nanotubes. PCDTBT:PC\(_71\)BM p–n junction composite nanotubes have better light absorption properties in a wide spectral range and
their bulk heterojunction films show an improved photo-induced charge transfer.

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Notes and references