Significantly Enhanced Photoluminescence of Doped Polymer-Metal Hybrid Nanotubes**

By Dong Hyuk Park, Hyun Seung Kim, Mi-Yun Jeong, Yong Baek Lee, Hyun-Jun Kim, Dae-Chul Kim, Jeongyong Kim, and Jinsoo Joo*

1. Introduction

Luminescence is an electron-excitation mechanism. This mechanism is accomplished by means of electrical current or optical absorption corresponding to electroluminescence (EL) and photoluminescence (PL), respectively.[1] Surface-plasmon resonance (SPR) based on metal nanostructures has been recently pursued in order to increase the PL efficiency. When the surface plasmon (SP) energy of a nanoscale metal matches the emitted photon energy of a light-emitting material, the resulting resonance can lead to an energy and/or charge transfer from the nanoscale metal surface to the light-emitting material or vice versa.[2] Therefore, this resonance can lead to a significant enhancement of the PL efficiency[3,4] which can be applied to applications in the fields of biological sensing, quantum wells or dots, light-emitting diodes, etc.[5–7] However, previous studies of the SP-enhanced PL have mainly focused on the energy-transfer effect.[5,8]

Since the first report of polymer-based organic light-emitting diodes (OLEDs) using poly(p-phenylene vinylene) (PPV),[9] many efforts have been made to study the light-emission mechanism and to improve the efficiency of the OLEDs. From the point of view of the active material for polymer-based OLEDs, morphological control of the polymer chain and the triplet-state emission for phosphorescence have been adopted to increase the light-emitting efficiency of OLEDs.[10–12] Recently, Barnes and coworkers reported that the light-emission efficiency of OLEDs could be increased by using a periodic microstructure to scatter waveguided[13] and hybrid nanostructures using nanoscale metal layers.[14] In general, the EL and PL efficiencies obtained using doped \( \pi \)-conjugated polymers or molecules are poor, because of scattering effects and/or PL quenching caused by the dopants or counterions. Therefore, pristine (i.e., undoped) organic \( \pi \)-conjugated materials have been used as the active material of most OLEDs. However, the PL efficiency of lightly doped polymers with discrete (that is, separated from conduction and valence bands) bipolaron bands can dramatically increase by means of a nanoscale metal coating, because of the charge transfer as well as the energy transfer in the SPR coupling.

In our previous study, we reported PL enhancement resulting from the energy transfer in the SPR coupling for a single strand of hybrid double-layered nanotubes (HDLNTs) fabricated using undoped polythiophene (PTh) nanotubes coated with nickel (Ni), copper (Cu), or cobalt (Co) metals.
The reported maximal increase of the PL intensity was \( \sim 70-100 \) times for the PTh/Ni single HDLNT strand.\[^{15}\] Here, we report on a significant enhancement in the PL intensity of a single strand of HDLNTs consisting of doped poly(3-methylthiophene) (P3MT) enveloped by nanoscale Ni metal, denoted as doped-P3MT/Ni. As the doping level of the P3MT nanotubes became higher, the PL intensity of the single strand of the P3MT/Ni HDLNTs increased remarkably, up to \( \sim 350 \) times. From the normalized UV-vis absorption spectra, we observed that on increasing the doping level of the P3MT nanotubes the new UV-vis absorption peaks corresponding to the SP energy of the HDLNTs of doped-P3MT nanotubes with nanoscale Ni coating increased, implying a charge transfer. The enhancement of the PL of the doped-P3MT-based HDLNTs was attributed to the effects of both energy transfer and charge transfer from the bipolaron band of the doped-P3MT materials in the SPR coupling. It should be noted that the P3MT material might be a better system than the PTh one for a study of the charge-transfer effect in SP-enhanced PL because of the stable formation of the doping-induced bipolaron states due to the methyl group.\[^{16}\]

2. Results and Discussion

2.1. Formation of Hybrid Double-Layered Nanotubes (HDLNTs) of P3MT/Ni

The HDLNTs of the P3MT/Ni material had a uniform and continuous array with a total diameter of \( \sim 200 \) nm, as shown in Figure 1a. From the magnified high-resolution transmission electron microscopy (HRTEM) images shown in the inset of Figure 1a, two different structural phases, that is, the crystalline phase in the outer part and the amorphous phase in the inner part, were clearly observed for the single strand of HDLNTs of P3MT/Ni. We performed an elemental analysis of the HDLNT through energy-dispersive spectroscopy (EDS) experiments during the measurements of the HRTEM images. In the inner part of the HDLNT, both sulphur (S) and Ni elements were detected, while only the Ni element existed in the outer part, as shown in Figure 1b. These results support the formation of the inner P3MT nanotube and outer Ni nanotube for the HDLNTs of P3MT/Ni. The thicknesses of the inner P3MT nanotube and outer Ni nanotube were both measured to be \( \sim 10 \) nm. Similar results were recently reported for the HDLNTs of polypyrrole with Ni and PTh with various Ni, Cu, or Co metals.\[^{15,27}\]

2.2. UV-Vis Absorption Spectra of Doped-P3MT Nanotubes

Figure 2 compares the normalized UV-vis absorption spectra of the P3MT nanotubes at different doping levels. The doping levels were controlled through an additional doping and dedoping process (see Experimental). The \( \pi-\pi' \) transition peaks were observed at \( \sim 385 \) nm for all of the P3MT nanotubes studied here. Broad bipolaron peaks due to doping were observed at near \( \sim 750-800 \) nm.\[^{18}\] Their relative intensity varied with the doping level, as shown in Figure 2. The relative-intensity ratio of the bipolaron peak to the \( \pi-\pi' \) transition peak for the doped-P3MT nanotubes was estimated as 0.67, 0.52, 0.25, and 0.04 depending on the degree of additional doping or dedoping. The relative-integrated-area ratio of the bipolaron peak to the \( \pi-\pi' \) transition peak was 0.67, 0.54, 0.22, and 0.01. Based upon the UV-vis absorption spectra, we denote the various doped-P3MT nanotubes studied here as the doped-P3MT(0.04), doped-P3MT(0.25), doped-P3MT(0.52), and doped-P3MT(0.67) nanotubes, where the number in brackets represents the relative doping level. The relatively small ratios
of intensity or area of the bipolaron peaks compared with those of the \( \pi-\pi^* \) transition peaks imply that the P3MT nanotubes studied here were lightly doped systems rather than heavily doped ones.

2.3. Laser Confocal Microscopy (LCM) PL Images and Spectra of Single Strands of Doped-P3MT and Doped-P3MT/Ni Nanotubes

Figure 3 compares the LCM PL images for an isolated single strand of doped-P3MT nanotubes with different doping levels and their HDLNTs enveloped by nanoscale Ni metal under the same LCM experimental conditions. The color bar with the unit of voltage at the left hand side of Figure 3 represents the measured LCM PL intensity. For the doped-P3MT nanotubes without the nanoscale Ni metal coating, the measured voltages of the LCM PL intensity of the doped-P3MT(0.04), doped-P3MT(0.25), doped-P3MT(0.52), and doped-P3MT(0.67) single nanotube strands were \( \sim 40–44 \text{ mV}, \sim 26–31 \text{ mV}, \sim 12–16 \text{ mV}, \) and \( \sim 5–8 \text{ mV} \), as shown in Figure 3(a–d), respectively. The results imply that the LCM PL intensity decreased on increasing the doping levels, which might originate from PL quenching by the dopant or the counterions in the doped-P3MT nanotubes. However, the upward tendencies of the LCM PL intensity for the single strand of the HDLNTs of doped-P3MT/Ni were dramatically reversed, through the nanoscale Ni metal coating. The measured voltages of the LCM PL intensity of the HDLNTs of the doped-P3MT(0.04)/Ni, doped-P3MT(0.25)/Ni, doped-P3MT(0.52)/Ni, and doped-P3MT(0.67)/Ni single nanotube strand were \( \sim 1.2–1.6 \text{ V}, \sim 1.8–2.1 \text{ V}, \sim 2.5–2.7 \text{ V}, \) and \( \sim 3.1–3.8 \text{ V} \), as shown in Figure 3(e–h), respectively. After the nanoscale Ni metal coating onto the doped-P3MT nanotubes, the measured voltages of the LCM PL intensity of the HDLNTs of doped-P3MT(0.67)/Ni with the highest doping level increased remarkably up to \( \sim 388–760 \) times, compared with those of the doped-P3MT(0.67) nanotube without the Ni coating (see Fig. 3d and Fig. 3h). The increase ratio of the measured voltages of the LCM PL intensity for the doped-P3MT(0.04)/Ni HDLNTs compared with those for the doped-P3MT(0.04) nanotube was the weakest at approximately \( \sim 27–40 \) times. The fluctuation of the measured voltages of the HDLNTs may originate from the inhomogeneous Ni coating and/or the oxidation of the Ni metal surface.[19]

The comparison of the LCM PL spectra of a single strand of the doped-P3MT nanotubes with various doping levels and...
their HDLNTs with the nanoscale Ni metal coating is shown in Figure 4. Figure 4a shows the LCM PL spectra of single strands of the doped-P3MT(0.04), doped-P3MT(0.25), doped-P3MT(0.52), and doped-P3MT(0.67) nanotubes. The peak intensity and the area of the LCM PL spectra of single strands of the P3MT nanotubes without the nanoscale Ni metal gradually increased up to 14 times as the doping level decreased, as shown in Figure 4a. Two characteristic peaks in the LCM PL spectra for the P3MT materials were observed at 640 nm and 685 nm. The small sharp peaks in the LCM PL spectra at 524 nm, 568 nm, and 620 nm are attributed to Raman modes. With the nanoscale Ni metal coating onto the P3MT nanotubes, the peak intensity and the integrated area of the LCM PL spectra significantly increased, as shown in Figure 4b. The upward tendencies of the increase of the LCM PL intensity were reversed, after the Ni coating. Compared to the LCM PL spectrum of the doped-P3MT(0.67) single nanotube, the LCM PL peak intensity at 685 nm for the HDLNTs of the doped-P3MT(0.67)/Ni increased up to \( \approx 350 \) times. The relative increases of the LCM PL peak intensity for the doped-P3MT(0.52)/Ni, doped-P3MT(0.25)/Ni, and doped-P3MT(0.04)/Ni HDLNTs were more than about 130, 35, and 10 times, respectively, compared with those for the doped-P3MT nanotubes without the nanoscale Ni metal coating. The relative increase of peak intensity (or integrated area) of the LCM PL spectra for the HDLNTs of P3MT/Ni and the P3MT nanotubes as a function of doping levels are shown in Figure 4c and its inset, respectively. The PL efficiency of the P3MT nanotubes without the nanoscale Ni metal coating decreased with increasing doping level, as shown in the inset of Figure 4c. However, when the doping level of the P3MT nanotubes increased, the PL efficiency of the HDLNTs of P3MT/Ni significantly increased, as shown in Figure 4c. It is noted that the doped-P3MT(0.67) nanotube is a reference material for the comparison of the PL efficiency in the inset of Figure 4c.

In order to analyze these results, we suggest that the charge-transfer effect in the SPR coupling contributed to the enhancement of the PL efficiency of the hybrid doped systems.

2.4. Fourier Transform Infrared (FTIR) and UV-Vis Absorption Spectra of Doped-P3MT and Doped-P3MT/Ni Nanotubes

In order to study the doped states of the doped-P3MT HDLNTs after the Ni metal coating, we measured Fourier transform infrared (FTIR) spectra of the systems. Figure 5a compares the FTIR spectra of doped-P3MT nanotubes with different doping levels. We observed characteristic IR vibration peaks for P3MT structures. Vibration peaks due to out-of-plane C-H deformation were observed at 620 cm\(^{-1}\) and 835 cm\(^{-1}\), and are associated with the \( \beta \) position of the 3-methylthiophene ring. The peak at 736 cm\(^{-1}\) corresponds to the out-of-plane C-H bending vibration at the \( \alpha \) position of the 3-methylthiophene ring. The methyl deformation C-H in-plane bending vibration peak and the ring-stretch vibration peak were observed at 1390 cm\(^{-1}\) and 1454 cm\(^{-1}\), respectively. For the doped-P3MT nanotubes, we observed doping-induced vibration peaks at about 975 cm\(^{-1}\), 1159 cm\(^{-1}\), 1200 cm\(^{-1}\), and 1302 cm\(^{-1}\). The intensity of the
doping-induced vibration peaks in the FTIR spectra increased with increasing doping level as shown in Figure 5a. Figure 5b compares the FTIR spectra of the HDLNTs of doped-P3MT/Ni with different doping levels. FTIR spectroscopy characteristic peaks for P3MT materials were also observed. The vibration peaks due to out-of-plane C-H deformation were observed at 617 cm$^{-1}$ and 831 cm$^{-1}$. The methyl deformation C-H in-plane bending vibration peak was observed at 1398 cm$^{-1}$. The aromatic-ring-stretch vibration peaks were observed at 1440 cm$^{-1}$, 1456 cm$^{-1}$, and 1518 cm$^{-1}$. Doping-induced vibration peaks of the doped-P3MT(0.67)/Ni and doped-P3MT(0.52)/Ni nanotubes were clearly observed at about 985 cm$^{-1}$, 1166 cm$^{-1}$, 1201 cm$^{-1}$, and 1317 cm$^{-1}$. Based on the results of the FTIR spectroscopy experiments, we can conclude that the doping states of the P3MT nanotubes remained after the Ni metal coating. Figure 5c compares the FTIR spectra of the doped-P3MT(0.67) nanotubes and the HDLNTs of the doped-P3MT(0.67)/Ni. We can directly observe the doping-induced vibration peaks and the slight shift of the peaks to higher wavenumber, for the P3MT nanotubes after the Ni metal coating. The intensities of the β-position-related vibration peaks at 617 cm$^{-1}$ and 831 cm$^{-1}$ and the methyl C-H in-plane bending of the HDLNTs of doped-P3MT(0.67)/Ni at 1398 cm$^{-1}$ increased after the Ni coating. The FTIR spectroscopy peak of the doped-P3MT(0.67)/Ni nanotubes at about 1700 cm$^{-1}$ could be assigned to the dangling bond or -OH group bonded to the thiophene rings after the Ni coating.[24,25] More details of the FTIR spectroscopy characteristic peaks of the doped-P3MT nanotubes and the HDLNTs of doped-P3MT/Ni are presented in the Supporting Information.

Figure 5. A comparison of the FTIR absorption spectra of a) the doped-P3MT nanotubes with different doping levels, b) the HDLNTs of the P3MT nanotubes with different doping levels enveloped by the Ni metal, and c) the doped-P3MT(0.67) nanotubes and doped-P3MT(0.67)/Ni nanotubes. The peaks with arrows represent the doping-induced ones.
charge-transfer effects from the doping-induced bipolaron states through the SPR coupling. Similar behavior had been reported for ZnO nanorod systems.\(^{[27]}\) Figure 6b shows the relative variation of the area of the SP peaks of the P3MT HDLNTs depending on the doping levels of the P3MT nanotubes, after the Ni metal coating. These were obtained from the peak decomposition of the UV-vis absorption spectra in Figure 6a. We observed a gradual increase of the area of the SP peaks at 563 nm and 615 nm of the P3MT HDLNTs after the nanoscale Ni metal coating, on increasing the doping level (i.e., the area of the bipolaron peaks at 800 nm) of the P3MT nanotubes. The results indicate the charge-transfer effect from the bipolaron band of the doped-P3MT nanotubes to the Ni metal, in the SPR coupling.

2.5. Energy-Band Diagram of Doped-P3MT/Ni Nanotubes

The energy gap of the undoped (i.e., pristine) P3MT material was measured to be 2.0 eV (\(\lambda_{\text{C}} \approx 620 \text{ nm}\)) and could be tuned up to about 2.33 eV (\(\lambda_{\text{C}} \approx 532 \text{ nm}\)) after a chemical doping.\(^{[28,29]}\) The energy-band diagram of the doped-P3MT material with the bipolaron band is schematically shown in the inset of Figure 7. We previously reported the UV-vis absorption peak at about 2.3 eV (\(\lambda_{\text{C}} \approx 541 \text{ nm}\)) for the Ni nanowires themselves, which were prepared through the same electrochemical deposition method.\(^{[15]}\) The skin depth of typical metals to allow light penetration should be of the order of 10 nm in the optical frequency range, which is similar to the thickness of the Ni nanotubes of the P3MT/Ni HDLNTs synthesized here.\(^{[15]}\) When a laser beam (\(\lambda_{\text{ex}} = 488 \text{ nm}\)) in the visible light range was incident on the outer nanoscale Ni metal of the hybrid P3MT/Ni nanotubes, the SPs were excited by the interaction between the incident laser beam and free charge carriers on the surface of the nanoscale Ni metal, and the laser beam could penetrate into the P3MT nanotubes for light emission. The SP energy (\(\sim 2.03-2.19 \text{ eV}\), equivalent to \(\lambda_{\text{C}} \approx 563-615 \text{ nm}\)) of the nanoscale Ni metal obtained from the results of Figure 6a closely matched the photon energy (\(\sim 2.0-2.3 \text{ eV}\)) of the light-emitting P3MT nanotubes. Then, the resulting resonance (the SPR coupling due to the hybrid junction of the P3MT and Ni nanotubes) could lead to energy transfer from the nanoscale Ni metal to the light-emitting P3MT nanotubes with the irradiating laser beam, which created more excitons in the light-emitting P3MT nanotubes, as shown in Figure 7. When the light-emitting P3MT nanotubes were in their doped states, the charge-transfer effect in the SPR coupling could be additionally involved, and was observed in Figure 6, through the matching of the \(E_{\text{F}}\) levels of the bipolaron band of the doped-P3MT and Ni nanotubes, as shown in Figure 7. Both energy- and charge-transfer (from the doping-induced charge-transfer effects from the doping-induced bipolaron states through the SPR coupling. Similar behavior had been reported for ZnO nanorod systems.\(^{[27]}\) Figure 6b shows the relative variation of the area of the SP peaks of the HDLNTs depending on the doping levels of the P3MT nanotubes, after the Ni metal coating. These were obtained from the peak decomposition of the UV-vis absorption spectra in Figure 6a. We observed a gradual increase of the area of the SP peaks at 563 nm and 615 nm of the P3MT HDLNTs after the nanoscale Ni metal coating, on increasing the doping level (i.e., the area of the bipolaron peaks at 800 nm) of the P3MT nanotubes. The results indicate the charge-transfer effect from the bipolaron band of the doped-P3MT nanotubes to the Ni metal, in the SPR coupling.

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bipolaron band) effects in the SPR coupling lead to a significant enhancement of the PL efficiency of the HDLNTs using the doped-P3MT nanotubes. Based on the results and analyses obtained in this study and the discussion by Lin et al., the schematic energy-band diagram explaining the PL enhancement of doped polymers through the SPR effect is shown in Figure 7.

2.6. Quantum Yield (ΦQY) of Doped-P3MT and Doped-P3MT/Ni Nanotubes

The quantum yield (ΦQY) of the HDLNTs of the doped-P3MT/Ni and the doped-P3MT nanotubes as a function of doping level is shown in Figure 8 and its inset, respectively. The ΦQY were obtained from Equation (1):

\[ \Phi_{QY} = \Phi_{ST} \left( \frac{Grad_X}{Grad_{ST}} \right) \left( \frac{\eta^2}{\eta_{ST}} \right) \]  

In Equation (1), the subscripts, ST and X, denote the standard sample (Coumarin 307) and the measured nanotubes, respectively. Grad means the gradient of the plot of the integrated fluorescence intensity versus absorbance and η is the refractive index of the solution. Compared with the ΦQY of the doped-P3MT(0.67) nanotubes without the Ni coating (ΦQY = 0.029), the ΦQY of the HDLNTs of the doped-P3MT(0.67)/Ni (ΦQY = 0.221) considerably increased, up to ~7.6 times. However, the ΦQY of the HDLNTs of the doped-P3MT(0.04)/Ni (ΦQY = 0.129) only increased by 1.3 times, compared with that of the doped-P3MT(0.04) nanotubes without the Ni coating (ΦQY = 0.102). On increasing the doping level, the ΦQY of the HDLNTs of the P3MT/Ni increased, while that of the doped-P3MT without Ni decreased, as shown in Figure 8 and its inset, respectively. These upward tendencies of the measured ΦQY as a function of doping level for the doped-P3MT nanotubes and their HDLNTs shown in the Figure 8 are similar to the results of the LCM PL intensities and spectra shown in Figure 4c, which confirms the significant enhancement of the PL efficiency for the doped-P3MT based HDLNTs.

3. Conclusions

In summary, HDLNTs consisting of doped P3MT with various doping levels and enveloped by nanoscale Ni metal were fabricated by a sequential electrochemical synthetic method. The doping levels of the P3MT nanotubes were controlled through additional doping and dedoping processes. Based on the results of FTIR-spectroscopy experiments, we observed that the doping states of the P3MT nanotubes remained after the Ni metal coating. From LCM PL experiments, as the doping levels of the P3MT nanotubes increased, the LCM PL intensity of the HDLNTs of doped-P3MT/Ni single nanotube strands dramatically increased, while that of the doped-P3MT nanotubes without Ni decreased. The LCM PL peak intensity of a single strand of the HDLNTs consisting of doped-P3MT(0.67) coated with nanoscale Ni metal was found to be enhanced ~350 times, compared with that of the doped-P3MT(0.67) single nanotube strand without Ni. The enhancement of the PL efficiency of the doped-P3MT-based HDLNTs was supported by quantum-yield measurements. From the normalized UV-vis absorption spectra of the HDLNTs, new, excited energy levels corresponding to the SP were created, and the intensity of the SP peak increased on increasing the doping level, indicating the charge-transfer effect. The broad bipolaron peaks were reduced after the Ni coating. The charge transfer, as well as the energy transfer, through the SPR coupling between the doped-P3MT nanotubes and Ni nanotubes contributed to the enhancement of the PL of the hybrid nanosystems. The SP-enhanced PL for the doped polymer-metal hybrid nanotube can be utilized for nanoscale optoelectronics, biological sensing, and organic-based displays.

4. Experimental

Sample Preparation: The coaxial HDLNTs consisting of the P3MT nanotubes enveloped by Ni metal nanotubes (P3MT/Ni) were fabricated through a sequential electrochemical synthetic method based upon an anodic alumina oxide (Al2O3) nanoporous template [17,19]. The Al2O3 nanoporous templates were purchased from Whatman Co. We used tetrabutylammonium hexafluorophosphate (TBAPF6) dopants for the electrochemical polymerization of the 3-methylthiophene (3MT) monomers. The 3MT monomers and TBAPF6 dopants were purchased from Sigma Aldrich Co. and used without further purification. The molar ratio of the monomer to dopant was 5:1. Based on these conditions, the doped-P3MT nanotubes were electrochemically synthesized. The electrochemical synthesis and solution PL characteristics of the light-emitting P3MT nanotubes were reported earlier [29]. We used cyclic voltammetry (CV) (Bioanalytical Systems Inc., EC Epsilon) for the electrochemical synthesis.

![Figure 8. Quantum yield (ΦQY) of the HDLNTs of doped-P3MT/Ni in CHCl3 solution as a function of doping level; inset: Quantum yield (ΦQY) of the doped-P3MT nanotubes in CHCl3 solution as a function of doping level.](image-url)
The doped-P3MT(0.52) (0.52 indicates the doping level) nanotube samples were obtained through the hydrofluoric acid (HF) treatment of the doped-P3MT nanotubes [29]. The additional doping and dedoping of the P3MT nanotubes were electrochemically controlled through the scan range of an applied potential of the CV. The additional doping and dedoping processes for the doped-P3MT nanotubes including the Al2O3 template (i.e., before the removal of the Al2O3 template) were performed in an acetonitrile (CH3CN) solution of 0.1 M 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) without 3MT monomers by using CV. We note that the BMIMPF6 dopant is an environmentally stable and recyclable ionic liquid that showed negligible loss of electroactivity. The applied potentials for additional doping and dedoping were approximately 0 to −1.0 V and 0 to 1 V, respectively. The 10 cycles of applied potential for the oxidation and reduction states were repeated to obtain the doped-P3MT(0.67) and the doped-P3MT(0.04) nanotubes, respectively. It is noted that the value of 0.04 for the doping level might indicate almost-dedoped states. The scan rate for the additional doping and dedoping processes was fixed at 20 mV s−1. For the doped-P3MT(0.25) nanotubes, the potential range for dedoping of the doped-P3MT(0.52) nanotube samples was −0.1 V to 1 V and 5 cycles of the reduction process were performed. The cyclic voltammogram in the first cycle exhibited a well-defined peak. The stable process was then performed by means of the BMIMPF6 ionic liquid. After the additional doping and dedoping for the doped-P3MT(0.07), doped-P3MT(0.25), and doped-P3MT(0.04) nanotubes, the Al2O3 template was removed by using the HF solvent.

For the HDLNTs of doped-P3MT/Ni nanotubes, the Ni metal with nanometer thickness (~10 nm) was directly coated potentiostatically at −1.0 V (versus Ag/AgCl) onto the surface of the doped-P3MT nanotubes, using the same batch of doped-P3MT nanotubes including the Al2O3 nanoporous template. For the electrochemical synthesis of the Ni nanotube, the electrolyte consisted of a solution of NiSO4·6H2O (270 g L−1) and NiCl2·6H2O (40 g L−1) with H3BO3 (40 g L−1) [15,19]. The applied bias for the Ni metal coating was −1 V for 20 min. The additional doping and dedoping process of the doped-P3MT/Ni nanotubes with the Al2O3 template was the same as the previous method for the doped-P3MT nanotubes. The Al2O3 template was removed by using the HF solvent. More details of the electrochemical synthesis of the nanotubes and the doping or dedoping process have been reported earlier [15-17,19,30].

Measurements: We visualized the formation of the HDLNTs of P3MT/Ni by using a field-emission scanning electron microscope (FE-SEM) (JEOL KSM-5200) and a high-resolution transmission electron microscope (HRTEM) (JEOL JEM-3010). The UV-vis (HP-8455) and FTIR (Nicolet 380) absorption spectra were measured for the analysis of the optical properties and doping states of the nanotubes, which were homogeneously dispersed in a chloroform (CHCl3) solution. For measuring the quantum yield (ΦQY) of the nanotubes dispersed in CHCl3 solution, the excitation wavelength was 400 nm. As a reference material for the measurement of ΦQY, Coumarin 307, dissolved in methyl alcohol (ΦQY = 0.89), was used.

The PL images and spectra for an isolated single strand of the P3MT nanotubes and the HDLNTs of P3MT/Ni were measured by using a home-made laser confocal microscope (LCM) built around an inverted optical microscope (Axiovert 200, Zeiss GmbH). Figure 9 shows a schematic diagram and photograph of the experimental set-up for the laser confocal microscope (LCM) experiment. We used an oil-immersion objective lens (Karl Zeiss, 63 x -NA 1.4) to focus the unpolarized laser light onto the isolated single strand of the nanotubes. The spot size of the focused laser beam on the sample was estimated to be about 190 nm. The scattered light was collected with the same objective lens and with the excitation laser light filtered out by a long-pass edge filter (Semrock). The red-shifted PL signal was focused to a multimode fiber (core size = 100 μm) that acted as a pinhole for the confocal detection. The other end of the multimode fiber was connected to a photomultiplier tube for the PL image or the input slit of a monochromator, 0.3 m in length, equipped with a cooled charge couple device for the LCM PL spectra measurement. Based on the process, we could perform the measurement of the LCM PL characteristics on the nanometer scale (less than 200 nm). The laser power and acquisition time incident on the sample for the LCM PL measurements were fixed at 35 μW and 1 s, respectively. More details for the LCM experiment have been reported previously [15,31].

Figure 9. Schematic diagram (top) and photograph (bottom) of the experimental set-up for the laser confocal microscope (LCM) experiment.

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