

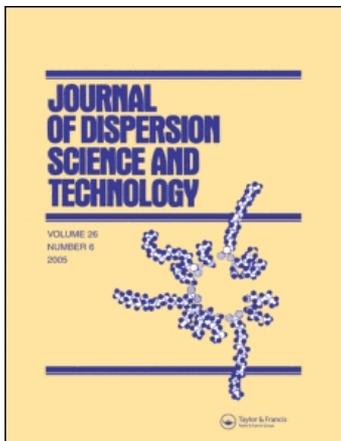
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### Noncovalent Functionalization of Single-Walled Carbon Nanotube by Porphyrin: Dispersion of Carbon Nanotubes in Water and Formation of Self-Assembly Donor-Acceptor Nanoensemble

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# Noncovalent Functionalization of Single-Walled Carbon Nanotube by Porphyrin: Dispersion of Carbon Nanotubes in Water and Formation of Self-Assembly Donor-Acceptor Nanoensemble

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Li Liang,<sup>1</sup> Dongmei Ren,<sup>1</sup> Yongsheng Chen,<sup>2</sup> and Jianyu Zheng<sup>1</sup>

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**A water-soluble nanoensemble of porphyrin and single-walled carbon nanotubes (SWNTs) was fabricated via electrostatic attraction. The formation of this supramolecular complex was monitored by UV-vis spectra and fluorescence spectra. The donor-acceptor properties of this nanoensemble were characterized by *I-V* performance of relative photovoltaic device fabricated by layer-by-layer (LBL) technique.**

**Keywords** Carbon nanotubes, nanoparticle dispersion, noncovalent functionalization, porphyrins

## INTRODUCTION

Single-walled carbon nanotubes (SWNTs) are being considered for many applications because of their unique mechanical and electrical properties. In order to overcome the strong intertube van der Waals interaction to improve their solvent dispersibility and endow SWNTs with new properties, various modification methods have been investigated.<sup>[1]</sup> Porphyrins (Por) are stable natural functional dyes with large  $\pi-\pi^*$  absorption bands in visible region and play important roles in photosynthesis and biocatalysis as they exhibit unique photophysical and electrochemical properties. Their properties can be controlled by different substituents and central metals and were often used as construction blocks for artificial solar energy conversion systems to mimic natural photosynthesis.<sup>[2]</sup> Due to the extensively conjugated two dimensional  $\pi$ -system and intense absorption in visible band, porphyrin is a good

electron donor and is suitable for efficient use of solar energy. Porphyrin-based chromophores act as antenna in plants to capture solar energy and convert it into chemical energy. So the combination of porphyrin and carbon nanotubes has drawn much attention since the first report by Nakashima and coworkers.<sup>[3]</sup> Some noncovalent and covalent SWNTs–Por systems have also been reported.<sup>[4,5]</sup>

Noncovalent functionalization is versatile in structure design and can maintain the integrity of nanotube's skeleton avoiding the disturbance of nanotube's electron structures induced by covalent functionalization, making the noncovalent method a facile and effective way to fabricate self-assembly SWNTs–Por supramolecular complex.<sup>[4]</sup> Among these systems, the synthesis of water-soluble complex is an important topic because such material is safe and inexpensive, and has potential applications in biomedicine. But surfactant and condensed aromatic compound with large  $\pi$ -systems, a kind of organic mutagenic carcinogen (e.g., pyrene), were often used to achieve the goal.<sup>[4]</sup> In this article, we describe facile prepared and environmental friendly aqueous self-assembly donor-acceptor system fabricated from water soluble cationic porphyrin noncovalent functionalized SWNTs (Figure 1). Through electrostatic layer-by-layer (LBL) method, we have fabricated a photovoltaic cell based on

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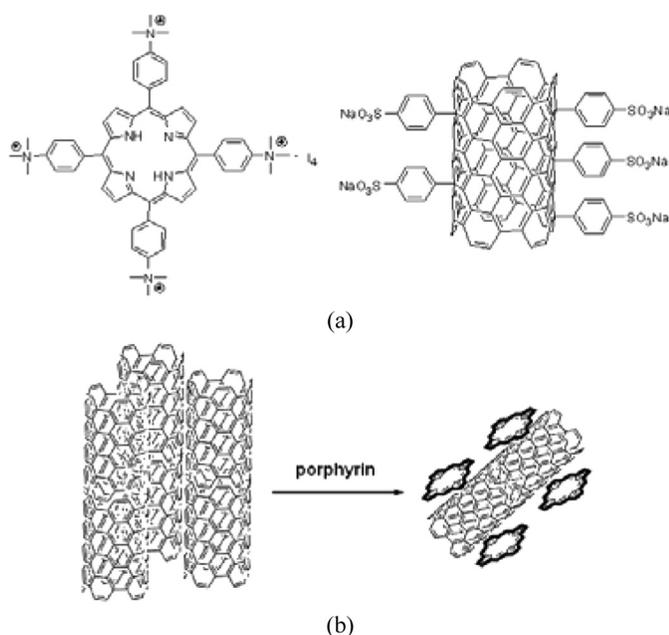


FIG. 1. (a) Structure of porphyrin and SWNTs discussed in this article. (b) Schematic representation of the formation of self-assembly nanoensemble.

this self-assembly nanoensemble and examined its photovoltaic properties.

## EXPERIMENTAL

### Measurements and Materials

NMR spectra were recorded with a Bruker spectrometer (AV300) at 300 MHz ( $^1\text{H}$  NMR) (Bruker, Germany). Chemical shifts were reported in ppm down field from internal  $\text{Me}_4\text{Si}$ . Mass spectra were acquired on a LCQ Advantage ESI ion trap spectrometer (ThermoFinnigan, USA). UV-Vis spectra were recorded on a Varian Cary 300 spectrophotometer using a quartz cell with a path length of 10 mm. Fluorescence spectra were obtained with a Varian Cary Eclipse fluorimeter (Varian, USA). Separations of SWNTs from the impurities were performed with a centrifuge (Eppendorf 5810R, Germany), and filtration was performed through a nylon membrane ( $0.2\ \mu\text{m}$ , 47 mm, Whatman International Ltd., UK). Water bath sonication was performed with a KQ-400KDE sonicator (400 W, 40 kHz, Kunshan Sonicor Instrument Co. Inc., China). Column chromatography was performed with silica gel (100–200 mesh, Qingdao Haiyang Chemical Co., Ltd. China). The current–voltage ( $I$ – $V$ ) measurement of the photovoltaic devices was conducted on a computer controlled Keithley 2400 Source Measure Unit. A Xenon lamp with AM 1.5 filter was used as the white light source, and the optical power at the sample was  $100\ \text{mW cm}^{-2}$ . Photovoltaic devices were fabricated in the ITO/SWNTs–Por/LiF/Al configuration. Indium tin oxide

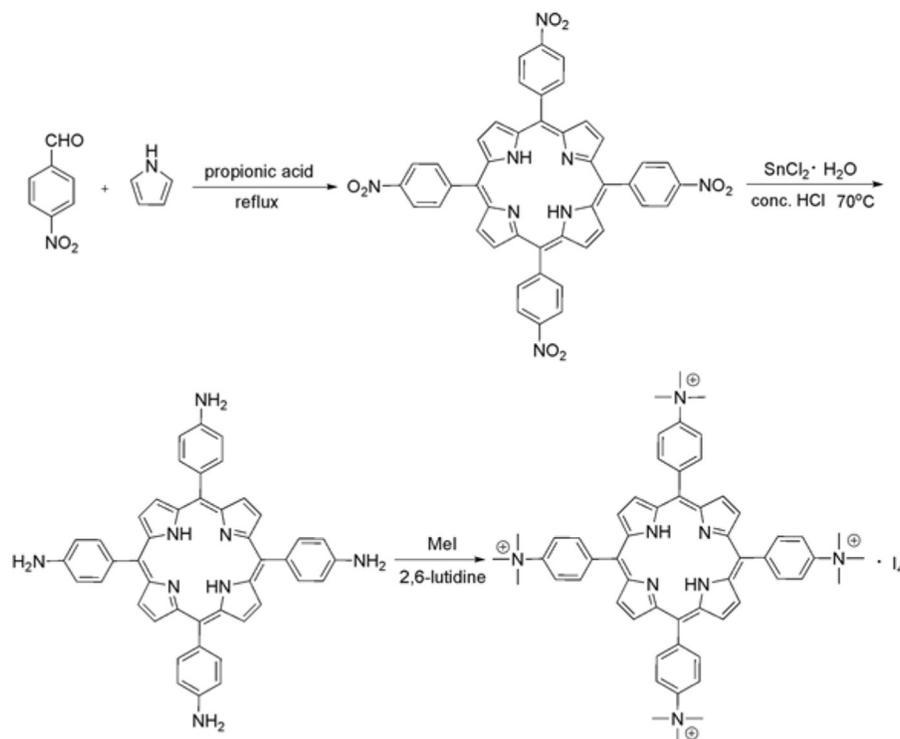
(ITO) coated glass,  $R_s = 10\ \Omega \cdot \text{square}^{-1}$ , was purchased from CSG Inc. LiF and Al was deposited on the active layer by vacuum evaporation under  $3 \times 10^{-4}\ \text{Pa}$ . Eight solar cell devices were fabricated in one cut ITO glass, and the effective area of each cell is  $4\ \text{mm}^2$ . Pristine SWNTs was synthesized and purified by reported methods.<sup>[6,7]</sup> Oleum (20% free  $\text{SO}_3$ ) was purchased from Shanghai No. 2 Zhenxing Chemical Plant (China). All aqueous solutions were made in deionized water.

### Synthesis of 5,10,15,20-Tetrakis(4-*N,N,N*-trimethylaminophenyl) Porphyrin Tetraiodide (Por<sup>+</sup>; Scheme 1)

An amount of 5.5 g 4-nitrobenzaldehyde (36.4 mmol) was dissolved in 150 mL of propionic acid and heated to reflux, then 6 mL acetic anhydride (6.43 g, 63.6 mmol) and 2.42 g freshly distilled pyrrole (36.2 mmol, dissolved in 5 mL of propionic acid) was added. After 24 hours the resulting solid was collected by filtration and washed with 40 mL of pyridine. After a thorough rinsing with acetone and air drying yielded 1.8 g of the solid product. The isolated porphyrin was directly used for reduction without any further purification. All the product (1.8 g) was dissolved in conc. HCl (37%, 250 mL) at  $70^\circ\text{C}$  and 15.0 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (66.4 mmol) was added. The mixture was stirred at  $70^\circ\text{C}$  for 7 hours and then cooled to room temperature. After neutralization with NaOH solution, the resulting crystalline product was collected by filtration and dissolved in acetone. Rotary evaporation of the solution followed by column chromatography (silica gel, eluent:  $V_{\text{ethyl acetate}}/V_{\text{acetone}} = 10/1$  to  $2/1$ ) yielded 5,10,15,20-tetrakis(4-aminophenyl)-21*H*,23*H*-porphine as a purple crystal. Yield: 1.2 g (20%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm):  $\delta$  –2.71 (s, 2H), 4.03 (s, 8H), 7.14–8.03 (m, 16H), 8.89 (s, 8H). ESI-MS ( $m/z$ ):  $\text{C}_{44}\text{H}_{35}\text{N}_8$  [ $\text{M} + \text{H}$ ]<sup>+</sup> calcd. 675.3, found 675.5. UV-vis ( $\text{CHCl}_3$ ,  $\lambda_{\text{max}}$ , nm): 427, 522, 562, 594, 654. 0.2 g 5,10,15,20-tetrakis(4-aminophenyl)-21*H*,23*H*-porphine (0.3 mmol), 2.4 g methyl iodide (16.9 mmol) and 0.26 g 2,6-lutidine (2.43 mmol) were dissolved in 10 mL DMF under nitrogen. The mixture was stirred under  $40^\circ\text{C}$  for 5 hours and then at room temperature overnight. The precipitate formed was filtered on a Buchner funnel and washed with acetone (30 mL). After drying under vacuum, the product was obtained as russet powder. Yield: 0.32 g (80%).  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 300 MHz, ppm):  $\delta$  3.87 (s, 36H), 8.19 (d,  $J = 8.7\ \text{Hz}$ , 8H), 8.33 (d,  $J = 8.4\ \text{Hz}$ , 8H), 8.90 (s, 8H). ESI-MS ( $m/z$ ):  $\text{C}_{56}\text{H}_{62}\text{N}_8$  [ $\text{M} - 4\text{I}$ ]<sup>4+</sup> calcd. 211.6, found 211.9. UV-vis ( $\text{H}_2\text{O}$ ,  $\lambda_{\text{max}}$ (log  $\epsilon$ ), nm): 412(5.66), 515(4.31), 549(3.98), 579(3.99), 631(3.75).

### Synthesis of Sulfonated SWNTs (SWNTs<sup>−</sup>; Scheme 2)<sup>[5,8]</sup>

Purified SWNTs (100 mg, p-SWNTs) were stirred in 100 mL oleum (20% free  $\text{SO}_3$ ) for 3 hours and then were heated to  $80^\circ\text{C}$ . An amount of 2.30 g sodium nitrite, 5.76 g sulfanilic acid, and 0.270 g AIBN were carefully



SCH. 1. Synthesis of 5,10,15,20-tetrakis(4-*N,N,N*-trimethylaminophenyl)porphyrin tetraiodide (Por<sup>+</sup>).

added. The system was stirred at 80°C for 2 hours and cooled. Then it was poured into 1.5 L of water (*Caution*: Severe heat release occurs and proper protection for eyes and face are needed) and filtered through a 0.2 μm nylon membrane. The filter cake was washed thoroughly with acetone and water. The obtained phenyl sulfonated SWNTs-SO<sub>3</sub>H (20 mg) were treated with NaOH solution (1 mol L<sup>-1</sup>, 30 mL) overnight at 80°C and then were diluted by 200 mL water. After filtered through a 0.2 μm nylon membrane and thoroughly washed with water, the product was redispersed in water by sonication and was centrifuged (2000 rpm, 3 minutes) to remove unreacted SWNTs. The supernatant product of SWNTs-SO<sub>3</sub>Na (SWNTs<sup>-</sup>) was collected by filtration and can be well dissolved in water with the help of sonication.

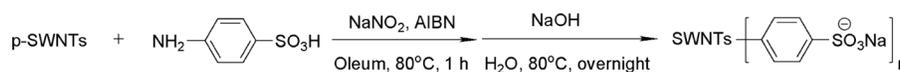
#### Preparation of Multilayer Films on Substrates

The quartz wafer was used as the substrate to monitor the self-assembly deposit process, which was cleaned by heating in a mixture of 30% H<sub>2</sub>O<sub>2</sub> and 98% sulfuric acid (1:3 in volume. *Caution*: The mixture is highly corrosive.) until no bubbles were released and then rinsing with

plentiful water. The ITO glass (2.5 × 2.5 cm<sup>2</sup>) was cleaned by ultrasonication with sodium dodecyl sulfate (SDS), water, acetone, followed by thoroughly washing with water and dried. These substrates were first immersed in aqueous cationic porphyrin solution (4.6 × 10<sup>-4</sup> mol L<sup>-1</sup>) for 1 hour to obtain a positively charged surface. Then rinsed with water and dried. Multilayer films on substrates were prepared by repeating the following steps: The substrate was first immersed in SWNTs<sup>-</sup> solution (0.24 g L<sup>-1</sup>) for 15 minutes, then washed with water and dried. After that it was immersed in Por<sup>+</sup> solution (4.6 × 10<sup>-4</sup> mol L<sup>-1</sup>) for 15 min, followed by rinsing with water and drying to complete an assembly cycle. In each cycle, a SWNTs/Por bilayer was fabricated on both sides of the wafer. For *I-V* measurement, 6 bilayers were deposited on ITO substrate. To eliminate the ineffective competitive absorption caused by the multilayers on back of the ITO electrode, films on the back were wiped off.

## RESULTS AND DISCUSSION

Sulfonated SWNTs was synthesized using diazotization-coupling procedure reported by Foley et al.<sup>[5]</sup> and was



SCH. 2. Synthesis of sulfonated SWNTs (SWNTs<sup>-</sup>).

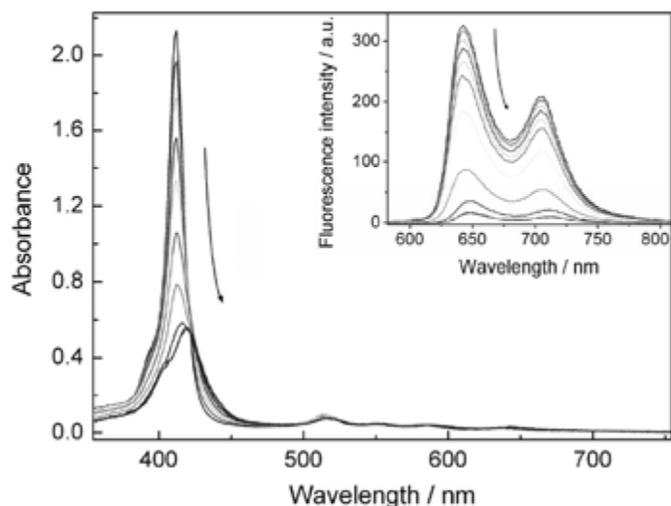


FIG. 2. Absorption spectra and fluorescence spectra changes (inset) of an aqueous solution of  $\text{Por}^+$  ( $4.7 \times 10^{-6} \text{ mol L}^{-1}$ ) upon titration on increasing addition of  $\text{SWNTs}^-$  in water (To subtract the absorption of  $\text{SWNTs}^-$  for clearly comparison, all absorption spectra have been normalized to zero absorbance at 800 nm; excitation wavelength is 411 nm).

converted to corresponding sodium salt<sup>[8]</sup> (abbreviated as  $\text{SWNTs}^-$ , Scheme 2). In aqueous solution, the positive-charged porphyrin attracts negative-charged  $\text{SWNTs}^-$  (Figure 1b), and then the formation of the supramolecular assembly of donor-acceptor complex was monitored by UV-vis spectra. As shown in Figure 2, the UV-vis spectra of 5,10,15,20-tetrakis(4-*N,N,N*-trimethylaminophenyl)porphyrin tetraiodide (abbreviated as  $\text{Por}^+$ ) in water show characteristic Soret and Q bands at 411 nm and 500~650 nm due to  $\pi-\pi^*$  transitions on the conjugated macrocycle. Upon titrated by variable amounts of  $\text{SWNTs}^-$ , the spectrum of porphyrin exhibits remarkable red shift of Soret and Q band (3~5 nm) and the intensity of corresponding absorbance decreased at the same time. The observed hypochromic and red shifts of porphyrin are caused by strong electrostatic and  $\pi-\pi$  interactions between  $\text{SWNTs}^-$  and  $\text{Por}^+$ , which is the characteristic of interactions between porphyrin and  $\pi$ -conjugated carbon materials (e.g.,  $\text{C}_{60}$ , carbon nanotube, carbon nanohorn).<sup>[9,10]</sup> The isosbestic point at 423 nm further convinces the efficient complexation of the two moieties. Figure 2 also shows the fluorescence spectra changes of  $\text{Por}^+$  during the titration. The emission of porphyrin at 642 and 704 nm decreased gradually upon the addition of  $\text{SWNTs}^-$  and shift progressively to the red with final maxima at 647 and 712 nm, which mirrors the changes in the ground state absorption spectra. The quenching is totally in accordance with the reported carbon nanotube/nanohorn/ $\text{C}_{60}$ -porphyrin systems and can be interpreted by effective photo-induced electron transfer from the excited state porphyrin to electron acceptor  $\text{SWNTs}^-$ .<sup>[4,11]</sup> The observations collectively suggest the formation of  $\text{SWNTs}^-$ - $\text{Por}$  nanohybrids.

In order to confirm the interensemble interaction mode, control experiment was carried out. An anionic porphyrin (tetrasodium 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, abbreviated as  $\text{Por}^-$ ) was titrated with  $\text{SWNTs}^-$  in stead of the cationic  $\text{Por}^+$ . However, the spectra of absorption and fluorescence were basically unchanged (Figure 3) indicating the repulsive electrostatic forces between the anionic nanotube and porphyrin broke off the intermolecular complexation of them. Thus, these results validate the electrostatic interaction play a core role in the formation of this supramolecular self assembly complex.<sup>[11]</sup>

Considering the efficient electron transfer between porphyrin and  $\text{SWNTs}$  and an intrinsic bulk heterojunction structure in this self-assembly donor-acceptor complex, we thus fabricated a photovoltaic device using this complex through electrostatically driven layer-by-layer (LBL) assembly technique.<sup>[12]</sup> Water soluble but oppositely-charged porphyrin and  $\text{SWNTs}$  were assembled alternately on the quartz glass or ITO-coated glass substrate via electrostatic attraction to form alternating multilayer films. This process was monitored with UV-vis spectroscopy of the films as shown in Figure 4. The alternating increase with an increasing numbers of layers in the absorbance at 426 nm of the Soret band (inset, Figure 4) indicates the quantitative formation of alternating multilayer films of  $\text{SWNTs}$  and porphyrin.

The current density-voltage  $I-V$  characteristics of the ITO/ $\text{SWNTs}$ - $\text{Por}$ /LiF/Al devices in dark and under white light illumination (AM 1.5,  $100 \text{ mW cm}^{-2}$  from the ITO side) are depicted in Figure 5. Under illumination, the hybrid device shows short circuit current density ( $I_{sc}$ ) of

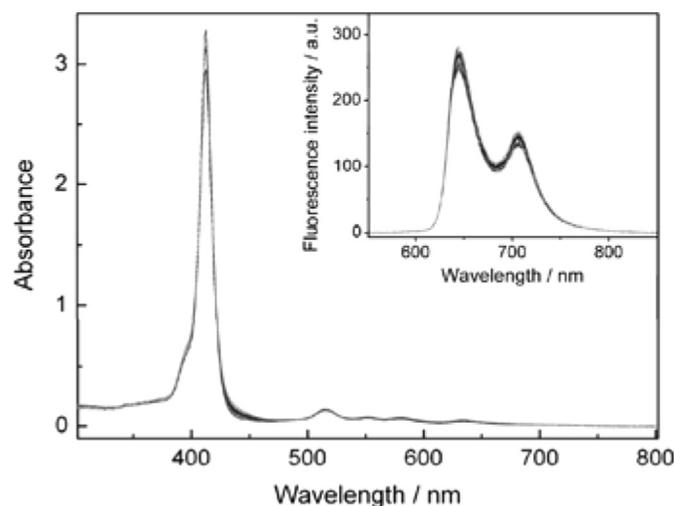


FIG. 3. Absorption spectra and fluorescence spectra (inset) changes of an aqueous solution of  $\text{Por}^-$  upon titration on increasing addition of  $\text{SWNTs}^-$  in water. (To subtract the absorption of  $\text{SWNTs}^-$  for clearly comparison, all absorption spectra have been normalized to zero absorbance at 800 nm; excitation wavelength is 413 nm).

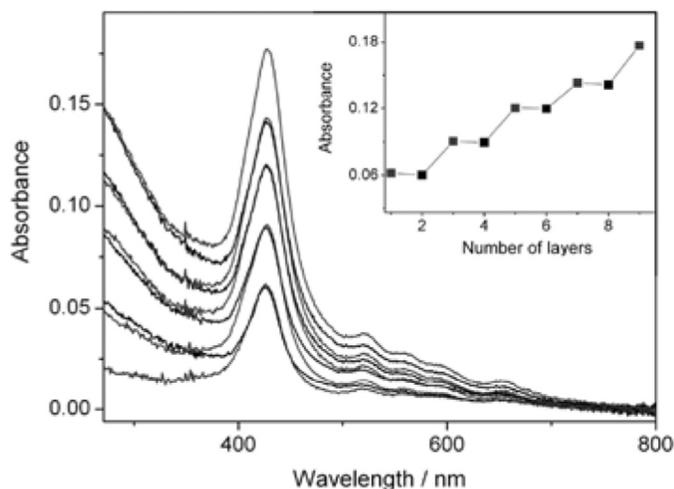


FIG. 4. Absorption spectra changes of films for the alternating layer-by-layer growth on the quartz substrate. The inset shows the plot of absorbance at 426 nm (porphyrin Soret band) versus the number of layers.

$23.7 \mu\text{A cm}^{-2}$  and an open circuit voltage ( $V_{oc}$ ) of 336 mV. The fill factor ( $FF$ ) is 0.24 and the power conversion efficiency was calculated to be  $1.9 \times 10^{-3}\%$ . Although it is comparatively low due to the inherent factors of the LBL films (e.g., relatively high resistance), this result is

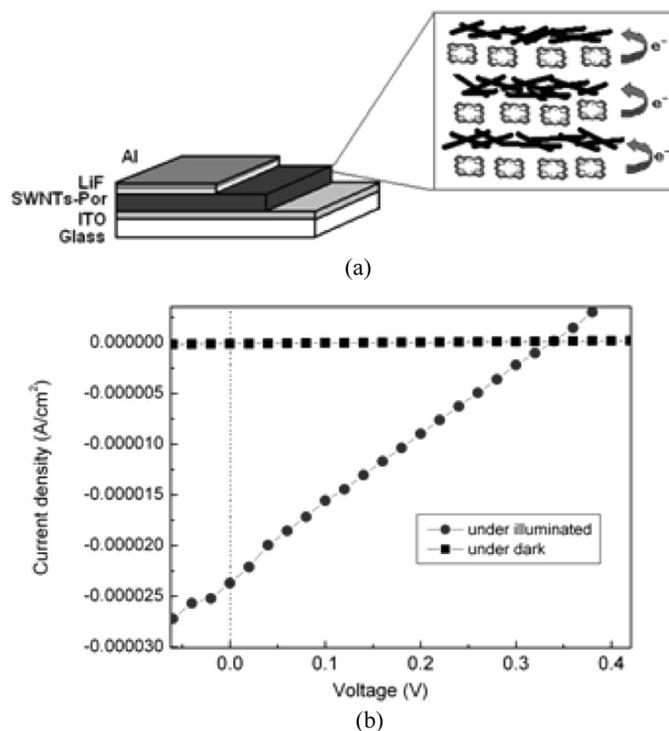


FIG. 5. a) Schematic representation of the photovoltaic cell and multilayer films formed by electrostatic LBL fabrication. b)  $I$ - $V$  curves of the ITO/SWNTs-Por/LiF/Al device measured in the dark and under illumination ( $100 \text{ mW/cm}^2$ ).

comparable with those of other photovoltaic cells using LBL approach and polymer/SWNTs systems.<sup>[13,14]</sup> In this hybrid device, the porphyrin act as light harvesting antenna and SWNTs play an important role in better dissociating excitons into electrons and holes and transporting electrons to electrode, which further proved the donor-acceptor properties of this nanoensemble and shows its potential of converting solar energy to electrical power.<sup>[15]</sup>

## CONCLUSION

In conclusion, these results provide a facile approach for the dispersion of carbon nanotube in water and pave the way toward the design and synthesize of CNTs based appealing and promising materials for safe, lower cost, and environmentally friendly optoelectronic and photovoltaic devices. To better understand the charge separation and transport characteristics mechanisms, further efforts are currently being undertaken.

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