Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 7510–7515
polymer
www.elsevier.com/locate/polymer

Covalent functionalization of multi-walled carbon nanotube surfaces by conjugated polyfluorenes

Guodong Xu, Bo Zhu, Yang Han, Zhishan Bo*

Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 11 September 2007; received in revised form 1 November 2007; accepted 4 November 2007
Available online 12 November 2007

Abstract

The outer surface of multi-walled carbon nanotubes (MWCNTs) was successfully modified with 7-bromo-9,9-dioctylfluorene-2-carbaldehyde by using 1,3-dipolar cycloaddition of azomethine reaction to introduce bromo functional groups. The peripheral bromo functional groups can be used to further react with AB-type monomers through Suzuki polycondensation to afford the PF-functionalized MWCNTs, which are of a cable-like structure. Through covalent connection to MWCNTs, the fluorescence of polyfluorenes was completely quenched by the MWCNTs, indicating a fast photo-induced electron transfer from polyfluorenes to MWCNTs.

Keywords: Carbon nanotubes; Conjugated polymers; Covalent functionalization

---

1. Introduction

Because of their unique structures, outstanding electrical and mechanical properties, and especially potential applications, carbon nanotubes (CNTs) have attracted considerable interest over the past few years [1–3]. It is still difficult to take their full advantages, since the pristine CNTs lack solubility in any solvent. Covalent and non-covalent modifications of the outer surface of CNTs have been proved to be successful methods to achieve soluble functional CNTs [4,5]. The non-covalent modification methods include the wrapping of CNTs with conjugated polymers and small organic dyes [6–13]. The covalent modification of the convex surfaces of CNTs by aliphatic molecules, organic functional molecules, atom transfer radical polymerization (ATRP) of vinyl monomers, and polyetherimide has been well documented in literature [4,5,14–23]. Additionally, single-walled and multi-walled CNTs have been used as n-type semiconductors to fabricate organic solar cells [22,24–26]. Baskaran et al. have successfully demonstrated MWCNTs and SWCNTs serving as an efficient electron acceptor that quenches the fluorescence of porphyrin covalently linked to CNTs [27]. During the preparation of this manuscript, there is one paper published on surface functionalization of single-walled nanotubes by Suzuki cross-coupling reactions [28].

Conjugated polymers are a novel class of semiconductors that have been found wide applications in many areas, such as organic light emitting diodes for flat panel displays, photovoltaic cells for solar energy conversion, thin-film transistors, and chemical sensors [29,30]. It would be of great interest to combine the advantages of carbon nanotubes and conjugated polymers. However, until now, the effective functionalization of CNTs with conjugated polymers is still a fascinating and challenging goal. The surface functionalized CNTs by conjugated polymers are of cable-like structures, with an n-type inner carbon nanotube layer and a p-type outer conjugated polymer layer. In a long term project, we hope that this kind of novel hybrid structures can be used to fabricate efficient organic solar cells. Here, we want to report an effective method to prepare such novel structure.

---

* Corresponding author. Tel./fax: +86 10 82618587.
E-mail address: zsbo@iccas.ac.cn (Z. Bo).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.11.012

2. Experimental section

2.1. Materials

The multi-walled carbon nanotubes were purchased from Shenzhen Nanotech Port Co., Ltd. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature, and stored in a Schlenk tube under nitrogen [31]. 7-Bromo-9,9-dioctyl-9*H*-fluorene-2-carbaldehyde was prepared according to the literature [32]. Solvents were dried according to standard procedures.

2.2. Instrumentation

Fourier transform infrared (FT-IR) spectra were recorded on a PE2000 spectrometer using the KBr disk method. ^1H NMR spectra were recorded on a Bruker AV400 spectrometer in $CDCl_3$. UV–vis absorption spectra were obtained on a Shimadzu UV–vis spectrometer model UV-1601 PC. Fluorescence spectra were recorded on a Varian-4500. Elemental analyses were performed on a Flash EA 1112 analyzer. TGA (TA2100) measurements were performed under nitrogen atmosphere at a heating rate of 20 °C/min. Scanning electron microscopic (SEM) images were obtained from Hitachi S-4300 electron microscope, and the samples were sputter-coated with a layer of homogeneous gold to facilitate charge dissipation during imaging. Transmission electron microscopy (TEM) was conducted using a JEM-2010 electron microscope at 200 kV. The samples for TEM were prepared by placing one drop of sample, previously ultrasonically dispersed in THF, on copper grids coated with carbon. The measurements of photocurrent responses were carried out on a CHI 630A Electrochemical Analyzer, and a 500 W xenon lamp was used as the light source. A three-electrode configuration consisting of a working electrode (ITO glass), a platinum wire counter electrode, and an Ag/Ag^+(0.1 M $AgNO_3$) reference electrode was used.

2.3. Acid-treated carbon nanotubes

In a typical experiment, crude MWCNTs (0.5 g) were added to 60% HNO_3 aqueous solution (60.0 mL). The mixture was treated with ultrasonic bath (40 kHz) for 10 min and stirred for 12 h at reflux. Then, the mixture was filtered through filter paper and washed with distilled water until the pH value of the filtrate was 7. The filtered solid was dried under vacuum for 24 h at ambient atmosphere, affording the acid-treated carbon nanotubes (0.42 g).

2.4. Synthesis of **1**

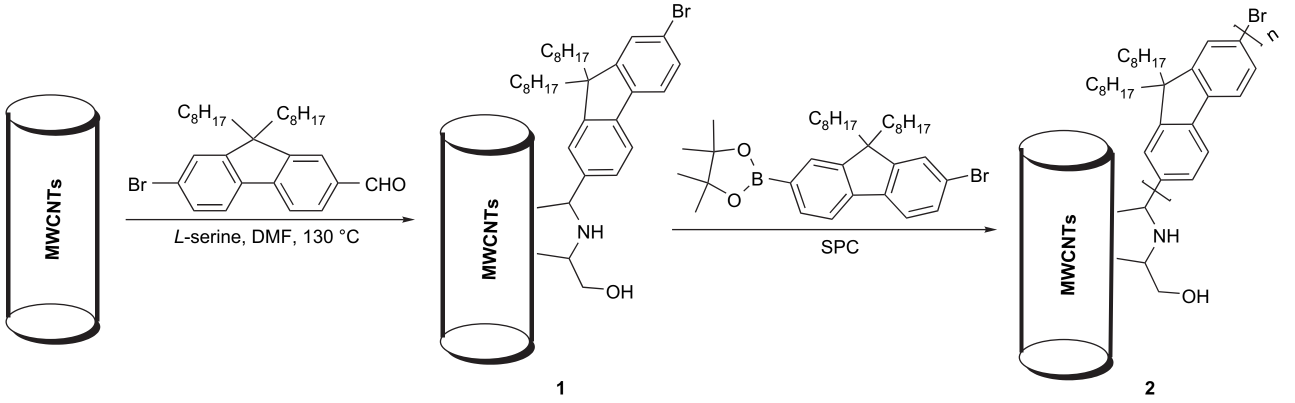
A mixture of MWCNTs (60 mg), 7-bromo-9,9-dioctyl-9*H*-fluorene-2-carbaldehyde (240 mg, 0.48 mol), L-serine (200 mg, 1.9 mmol), and DMF (50 mL) was stirred at 130 °C under nitrogen for 3 days. After the reaction, the mixture was filtered by filter paper and washed thoroughly with H_2O and THF. The crude MF-functionalized MWCNTs were further purified by Soxhlet extraction with THF and dried under high vacuum to afford **1** (65 mg) as a dark-grey solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.25–1.18 (br), 0.83 (br). The bromo content of **1** determined by EA is 1.08.

2.5. Synthesis of **2**

A mixture of **1** (30 mg), 2-bromo-9,9-dioctylfluorenyl-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (600 mg, 1.0 mmol), $NaHCO_3$ (1.27 g, 15 mmol), $Pd(PPh_3)_4$ (23 mg, 20 μmol), THF (30 mL), and water (10 mL) was carefully degassed and charged with nitrogen. The mixture was stirred and refluxed for 72 h. The mixture was filtered using filter paper and washed thoroughly with H_2O and THF. The crude product was further purified by Soxhlet extraction with THF and dried under high vacuum to afford **2** (36 mg) as a grey solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.25–1.04 (br), 0.83 (br). The bromo content of **2** determined by EA is 0.42.

3. Results and discussion

The synthetic routes for the functionalization of MWCNTs with conjugated polyfluorenes (PFs) are shown in Scheme 1. 1,3-Dipolar cycloaddition of azomethine (Prato) reaction was used to modify the outer surface of the purified MWCNTs. The reaction of 7-bromo-9,9-dioctylfluorene-2-carbaldehyde, L-serine, and MWCNTs in DMF at 130 °C for 3 days afforded



Scheme 1. Synthesis of the PF-functionalized MWCNTs.

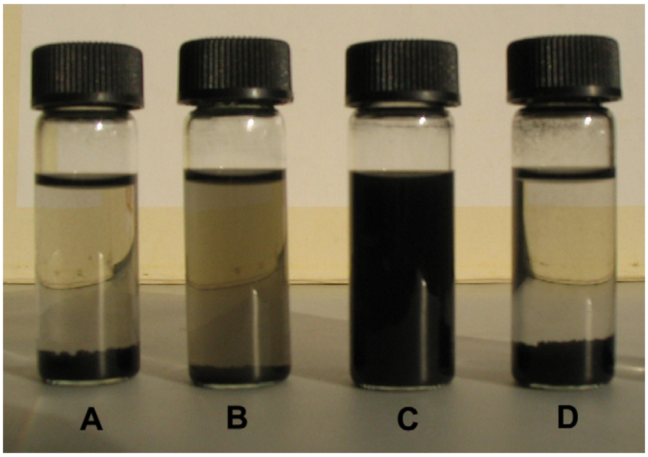


Fig. 1. Photographs of the acid-treated MWCNT (A), **1** (B), **2** (C), and the acid-treated MWCNTs/PF (D) dispersed in THF.

the mono-fluorene-modified MWCNTs **1**. The surface functionalization of MWCNTs with 7-bromo-9,9-dioctylfluorene units not only brings about functional bromo groups, but also endows the MWCNTs with slightly better solubility in common organic solvents. The growth of conjugated polyfluorene chains on the surfaces of MWCNTs was achieved by the polycondensation of **1** and 2-(2-bromo-9,9-dioctylfluoren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in a biphasic system (THF/aqueous $NaHCO_3$) with freshly prepared $Pd(PPh_3)_4$ as a catalyst precursor. The PF-functionalized MWCNTs **2** were purified by filtration and washed thoroughly with water and THF until no free polyfluorene can be detected by fluorescence spectroscopy in the filtrate to afford **2** as a dark-grey solid. Compared with the acid-treated MWCNTs, the polyfluorene-modified MWCNTs **2** displayed much better dispersibility in common organic solvents, such as THF and toluene. As shown in Fig. 1, only the PF-functionalized

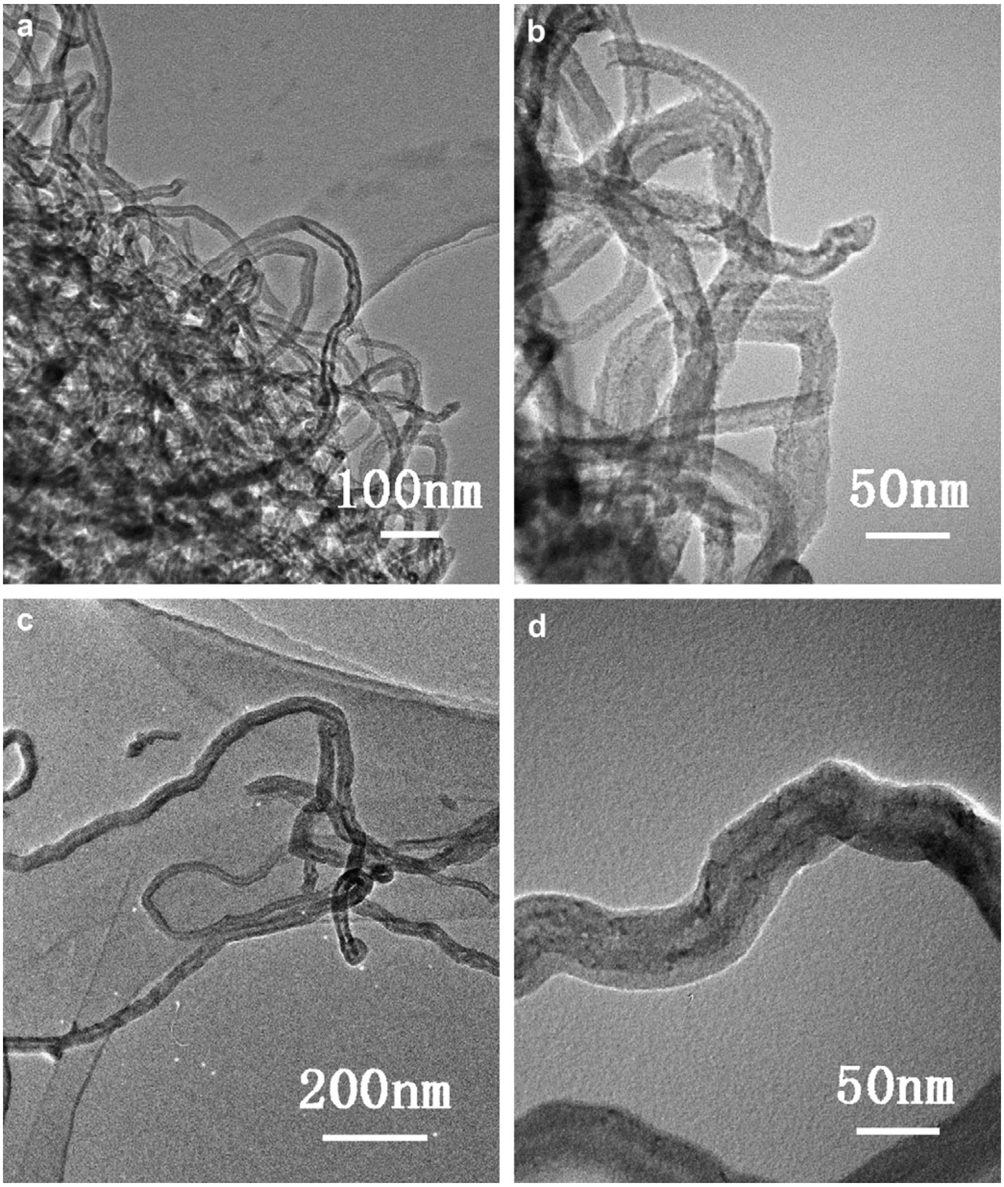


Fig. 2. TEM images of the acid-treated MWCNTs at low magnification (a) and at high magnification (b), **2** at low magnification (c) and at high magnification (d).

MWCNTs **2** in THF formed a stable solution after ultrasonication and allowed to stand 3 days. The acid-treated MWCNTs, mono-fluorene-modified MWCNTs **1**, and a mixture of the acid-treated MWCNTs and polyfluorenes in THF did not form a stable solution under the same conditions.

Combustion analysis revealed that the bromo content of **1** was 1.08%. We could roughly estimate that per 570 carbon atoms of the MWCNTs carries one fluorene unit from the composition "$C_nC_{32}H_{46}BrNO$". For **2**, the bromo content decreased to 0.42%. A polymerization degree of 26 for polyfluorenes grafted on the surface of MWCNTs is roughly estimated according to the composition "$C_{570}C_{32}H_{46}BrNO(C_{29}H_{40})_m$". Transmission electron microscopy (TEM) was used to investigate the structures of the acid-treated MWCNTs, **1**, and **2**, and the results are shown in Fig. 2. Fig. 2(a) and (b) shows the acid-treated MWCNTs in large scale at low magnification and several carbon nanotubes at high magnification, respectively. From the TEM images, we could clearly see that the amorphous carbons and catalytic residues were completely removed. The acid-treated MWCNTs are of tubular structure with an average diameter ranging from 15 to 30 nm. They are prone to conglomeration in the organic solvents used to disperse them. Fig. 2(c) and (d) shows the covalent functionalized MWCNTs **2** at low and high magnifications, respectively. From the high resolution image, it can be easily observed that polyfluorene functionalized MWCNTs **2** have an average diameter of 30–50 nm and a polyfluorene layer of about 11 nm in thickness. Fig. 3 shows the FT-IR spectra of the acid-treated MWCNTs, **1**, and **2**. It can be clearly seen that after functionalization with fluorene monomer and polymer, new absorption peaks at 2921 and 2852 cm^{-1} appeared, which are from the methyl and methylene groups on the side chains of fluorene units. The broad absorption band peaked at 3430 cm^{-1} of **1** and **2** was due to the hydroxyl groups.

The thermal properties of the acid-treated MWCNTs, **1**, **2**, and poly(9,9-dioctylfluorene)s (PF)s were investigated by TGA and the results are shown in Fig. 4. The acid-treated MWCNTs exhibited very good thermal stability. Under nitrogen atmosphere, they showed 4 and 8% weight losses at 400 and 600 °C, respectively. For mono-fluorene-functionalized MWCNTs **1**, they displayed a 15% weight loss at 600 °C. The PF-functionalized MWCNTs **2** started to decompose at about 150 °C and lost about 50% of their weight at 600 °C. For comparison, PF without bromo endgroups exhibited good thermal stability under 400 °C (less than 5% weight loss) and lost 60% of its weight at 600 °C. The TGA weight loss curve of the PF-functionalized MWCNTs **2** is similar to that of the bromo-terminated conjugated polymers [33–35]. The low decomposition temperature of the PF-functionalized MWCNTs **2** is due to the bromo endgroups of the grafted polyfluorenes. In our previous works [33–35], we have found that the bromo endgroups could dramatically decrease the decomposition temperature of conjugated polymers. The weight loss is mainly due to the partial decomposition of the outside fluorene moieties. The worse stability of **2** than **1** is simply due to that the fluorene content of **2** is much higher than that of **1**. From the TGA weight loss curves, we can conclude that the weight loss of the PF-functionalized carbon nanotubes from 150 to 600 °C is mainly due to the decomposition of the grafted polymers on carbon nanotubes. Since the decomposition of polyfluorene itself also leaves about 40% weight of char, it is difficult to calculate the exact content of polyfluorene in the PF-functionalized carbon nanotubes **2**.

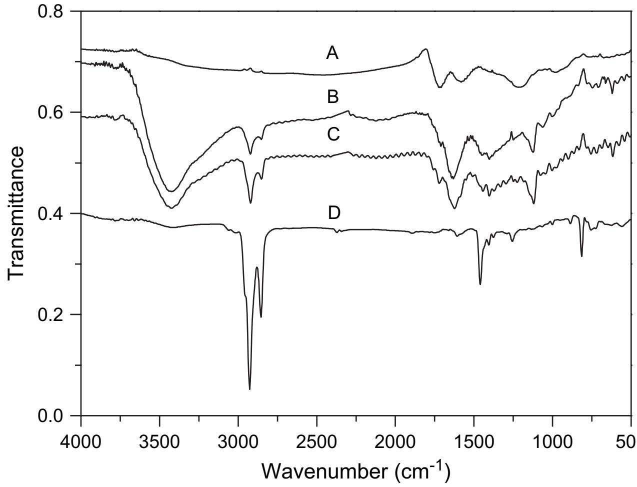


Fig. 3. FT-IR spectra of the acid-treated MWCNTs (A), the mono-fluorene-functionalized MWCNTs **1** (B), the PF-functionalized MWCNTs (C), and polyfluorene (D).

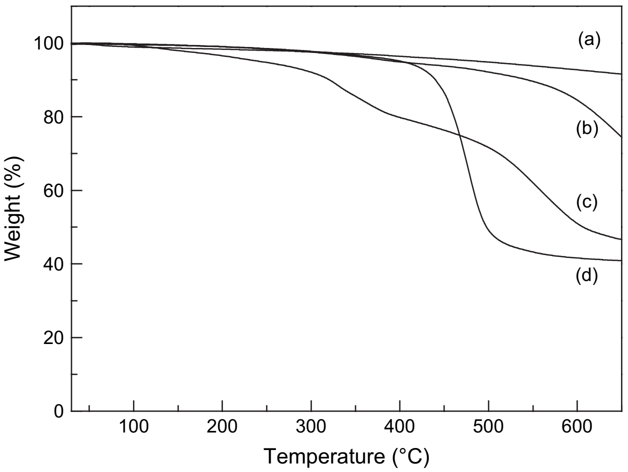


Fig. 4. TGA curves of the acid-treated MWCNTs (a), **1** (b), **2** (c), and PF (d).

Many conjugated polymers can be physically absorbed on the surface of multi-walled carbon nanotubes. To confirm that polyfluorene is not physically absorbed, but attached to the surface by chemical bond, optical property studies were therefore carried out. Five samples (the acid-treated MWCNTs, **1**, **2**, acid-treated MWCNTs/PF, and PF in THF solutions) were investigated by UV–vis absorption and fluorescence emission spectroscopies. The concentration of PF in two samples (MWCNTs/PF and PF) is at a concentration that PF can only be detected by fluorescence but not by UV–vis absorption spectroscopy. It is well known that the detection limit of fluorescence emission spectroscopy is much lower than that of UV-absorption spectroscopy. In the UV-

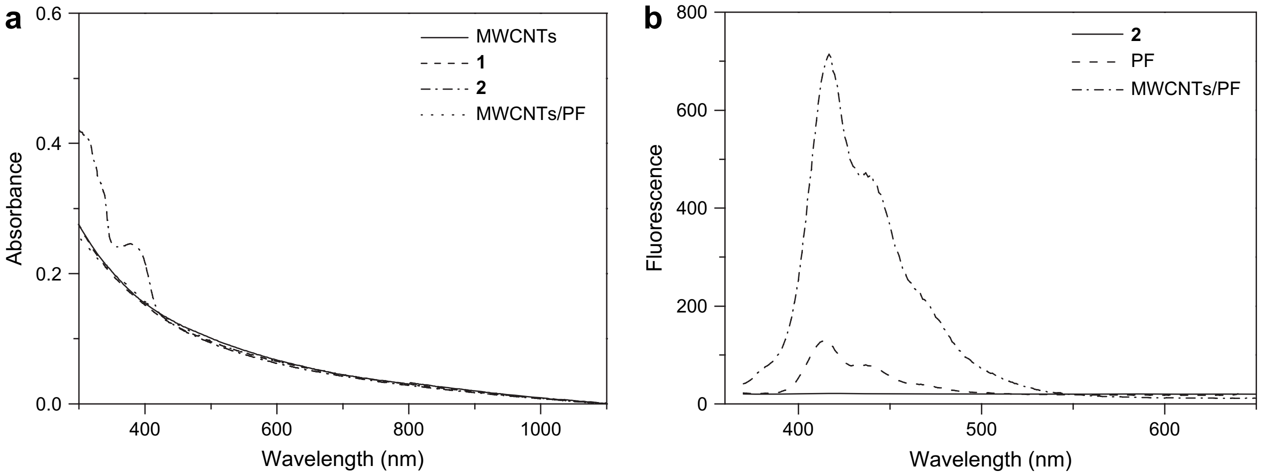


Fig. 5. (a) UV–vis absorption spectra of MWCNTs, the mono-fluorene-functionalized MWCNTs **1**, the PF-functionalized MWCNTs **2**, and the acid-treated MWCNTs/polyfluorene (MWCNTs/PF) dispersed in THF. (b) Photoluminescent spectra of polyfluorene, the PF-functionalized MWCNTs **2**, and the acid-treated MWCNTs/polyfluorene (MWCNTs/PF) dissolved or dispersed in THF.

absorption spectra shown in Fig. 5a, it can be clearly seen that for the PF-functionalized MWCNTs **2** there are two additional peaks at 350–400 nm, originated from the absorption of conjugated polyfluorene chains. No absorption spectrum can be obtained for PF and the acid-treated MWCNTs/polyfluorene (MWCNTs/PF), since the concentration of PF in these samples is below the detection limit of UV spectroscopy. The same samples were also used for fluorescence spectroscopic measurement. The fluorescence spectra of **2**, PF, and a mixture of the acid-treated MWCNTs and polyfluorenes (MWCNTs/PFs) are shown in Fig. 5b for comparison. In THF solution, polyfluorene emitted light in the blue region with two peaks at 414 and 436 nm and a shoulder at 466 nm, whereas in the case of **2**, the emission of polyfluorenes grafted on the surface of MWCNTs was completely quenched by the MWCNTs. Control experiment was done by using a mixture solution of the acid-treated MWCNTs and PF (MWCNTs/PF). The concentration of PF in this sample is very low, which cannot be detected by UV-absorption spectroscopy. However, the blue fluorescence of PF in MWCNTs/PF cannot be quenched efficiently by the MWCNTs. The optical property studies clearly show that the emission of PF cannot be effectively quenched by multi-walled carbon nanotubes if PF is not chemically bonded to the nanotubes. The strong absorption and very weak fluorescence emission of **2** indicate that PF is chemically attached to multi-walled carbon nanotubes.

The photo-induced electron transfer and the semiconducting properties of the polyfluorene-modified MWCNTs were also investigated. Films on ITO substrates used for photocurrent response measurements were prepared by spin-coating with a 10 mg/mL dispersion of **2** or the acid-treated MWCNTs in toluene at 1000 rpm. Fig. 6 shows the photocurrent response curve of the PF-functionalized MWCNT film and the acid-treated MWCNT film in photoelectrochemical cells. For the PF-functionalized MWCNT film, as shown in Fig. 6a, the photocurrent response was prompt and reproducible during repeated on/off cycles of the visible light illumination, whereas for the acid-treated MWCNT film, as shown in

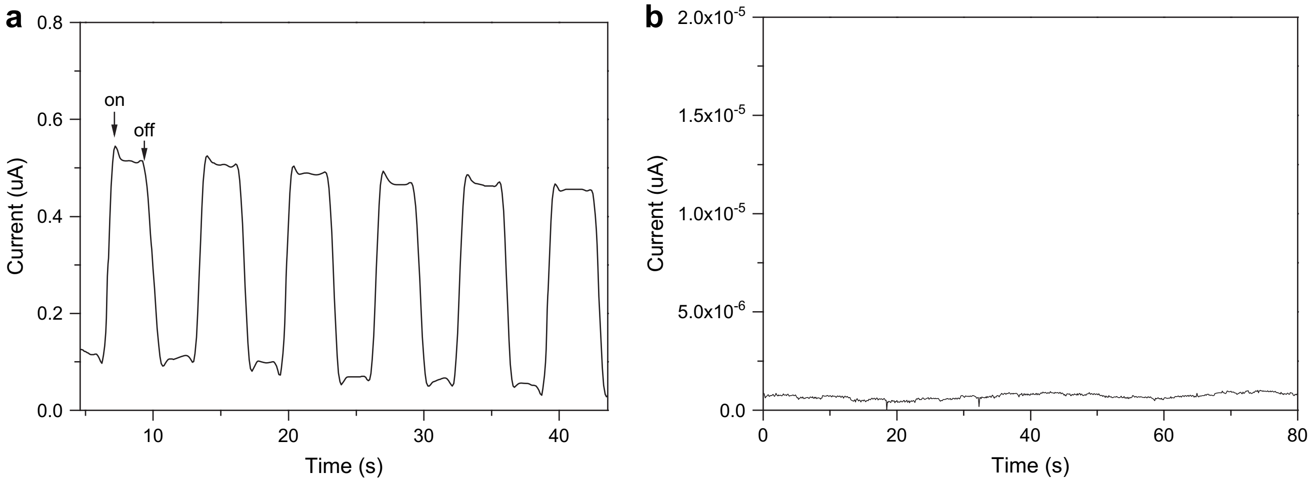


Fig. 6. Photocurrent responses of **2** (a) and the acid-treated MWCNT (b) films at zero bias in aqueous 0.1 M KCl solution.

Fig. 6b, no photocurrent response could be observed under visible light irradiation. Clearly, the PF chains grafted on the outer surface of MWCNTs are responsible for the photo-induced electron transfer.

In summary, we have successfully functionalized MWCNTs with 7-bromo-9,9-dioctylfluorene-2-carbaldehyde by using 1,3-dipolar cycloaddition of azomethine reaction to introduce bromo functional groups on the surfaces of MWCNTs. The peripheral bromo functional groups can be further modified by SPC with AB-type monomers to afford the desired PF-functionalized MWCNTs, which are of a cable-like structure. Through covalent bond connected to the MWCNTs, the fluorescence of polyfluorenes was completely quenched by the MWCNTs, indicating a fast photo-induced electron transfer from polyfluorenes to MWCNTs. The use of PF-functionalized MWCNTs for photovoltaic application is in progress.

Acknowledgment

Financial support by the National Natural Science Foundation of China (20574075, 20423003 and 50521302) is gratefully acknowledged.

References

[1] Zhang M, Fang SL, Zakhidov AA, Lee SB, Aliev AE, Williams CD, et al. Science 2005;309:1215–9.

[2] Wu ZC, Chen ZH, Du X, Logan JM, Sippel J, Nikolou M, et al. Science 2004;305:1273–6.

[3] Dalton AB, Collins S, Munoz E, Razal JM, Ebron VH, Ferraris JP, et al. Nature 2003;423:703.

[4] (a) Tasis D, Tagmatarchis N, Bianco A, Prato M. Chem Rev 2006; 106:1105–36;
(b) Guldi DM, Rahman A, Sgobba V, Ehli C. Chem Soc Rev 2006; 35:471–87.

[5] Chen J, Liu HY, Weimer WA, Halls MD, Waldeck DH, Walker GC. J Am Chem Soc 2002;124:9034–5.

[6] Satake A, Miyajima Y, Kobuke Y. Chem Mater 2005;17:716–24.

[7] Ehli C, Rahman GMA, Jux N, Balbinot D, Guldi DM, Paolucci F, et al. J Am Chem Soc 2006;128:11222–31.

[8] Curran SA, Ajayan PM, Blau WJ, Carroll DL, Coleman JN, Dalton AB, et al. Adv Mater 1998;10:1091–3.

[9] Coleman JN, Dalton AB, Curran S, Rubio A, Davey AP, Drury A, et al. Adv Mater 2000;12:213–6.

[10] Tang BZ, Xu HY. Macromolecules 1999;32:2569–76.

[11] Yuan WZ, Sun JZ, Dong YQ, Haussler M, Yang F, Xu HP, et al. Macromolecules 2006;39:8011–20.

[12] Star A, Stoddart JF, Steuerman D, Diehl M, Boukai A, Wong EW, et al. Angew Chem Int Ed Engl 2001;40:1721–5.

[13] Steuerman DW, Star A, Narizzano R, Choi H, Ries RS, Nicolini C, et al. J Phys Chem B 2002;106:3124–30.

[14] Ge JJ, Zhang D, Li Q, Hou HQ, Graham MJ, Dai LM, et al. J Am Chem Soc 2005;127:9984–5.

[15] Li SP, Qin YJ, Shi JH, Guo ZX, Li YF, Zhu DB. Chem Mater 2005; 17:130–5.

[16] Kong H, Gao C, Yan DY. J Am Chem Soc 2004;126:412–3.

[17] Yao ZL, Braidy N, Botton GA, Adronov A. J Am Chem Soc 2003; 125:16015–24.

[18] Kong H, Li WW, Gao C, Yan DY, Jin YZ, Walton DRM, et al. Macromolecules 2004;37:6683–6.

[19] Xu YY, Gao C, Kong H, Yan DY, Jin YZ, Watts PCP. Macromolecules 2004;37:8846–53.

[20] Kong H, Gao C, Yan DY. Macromolecules 2004;37:4022–30.

[21] Gao C, Vo CD, Jin YZ, Li WW, Armes SP. Macromolecules 2005;38: 8634–48.

[22] Bhattacharyya S, Kymakis E, Amaratunga GAJ. Chem Mater 2004; 16:4819–23.

[23] Liu YQ, Adronov A. Macromolecules 2004;37:4755–60.

[24] Xu ZH, Wu Y, Hu B, Ivanov IN, Geohegan DB. Appl Phys Lett 2005; 87:263118–20.

[25] Kymakis E, Alexandrou I, Amaratunga GAJ. J Appl Phys 2003;93: 1764–8.

[26] Kymakis E, Amaratunga GAJ. Appl Phys Lett 2002;80:112–4.

[27] Baskaran D, Mays JW, Zhang XP, Bratcher MS. J Am Chem Soc 2005; 127:6916–7.

[28] Cheng FY, Adronov A. Chem Mater 2006;18:5389–91.

[29] Hide F, DiazGarcia MA, Schwartz BJ, Heeger AJ. Acc Chem Res 1997;30:430–6.

[30] McQuade DT, Pullen AE, Swager TM. Chem Rev 2000;100:2537–74.

[31] Tolman CA, Seidel WC, Gerlach DH. J Am Chem Soc 1972;94:2669–74.

[32] Li BS, Li J, Fu YQ, Bo ZS. J Am Chem Soc 2004;126:3430–1.

[33] Sun MH, Bo ZS. J Polym Sci Part A Polym Chem 2007;45:111–24.

[34] Sun MH, Li J, Li BS, Fu YQ, Bo ZS. Macromolecules 2005;38:2651–8.

[35] Xu GD, Han Y, Sun M, Bo ZS, Chen CH. J Polym Sci Part A Polym Chem 2007;45:4696–706.