

## 功能化碳纳米管与四苯基锌卟啉轴向配位组装

佟履冰 姜 李 孙 剑 尹 桂\*

(南京大学化学化工学院, 南京 210093)

**摘要:** 本文报道了一种基于四苯基锌卟啉与含吡啶基功能化多壁碳纳米管经轴向配位组装。它们被红外光谱、拉曼光谱和透射电镜所表征。荧光光谱研究表明, 在该体系中功能化多壁碳纳米管能有效地淬灭卟啉的荧光。

**关键词:** 多壁碳纳米管; 卟啉; 轴向配位; 荧光

中图分类号: O613.71

文献标识码: A

文章编号: 1001-4861(2010)11-1939-05

## Supramolecular Self-assembly of Zinc Tetraphenylporphyrin with Functionalized Multi-walled Carbon Nanotubes via Axial Coordination

TONG Lü-Bing JIANG Li SUN Jian YIN Gui\*

(School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093)

**Abstract:** Functionalized multi-walled carbon nanotubes (MWCNTs) containing pyridyl group were prepared and characterized by Fourier transform-infrared spectra, Raman spectra and transmission electron microscope. The interaction between the functionalized MWCNTs and zinc tetraphenylporphyrin via axial coordination was investigated by UV-Vis and fluorescence emission spectra. MWCNTs can effectively quench fluorescence of ZnTPP via axial coordination.

**Key words:** multi-walled carbon nanotubes; zinc tetraphenylporphyrin; axial coordination; fluorescence

Since the discovery of carbon nanotubes (CNTs) in 1991<sup>[1]</sup>, they have attracted much attention because of their remarkable optical, electrical, and mechanical properties and potential applications in various fields including nanodevices, field effect transistors, full-color displays, sensors, ultrafast optical switches, engineering fibers and catalyst supports<sup>[2-4]</sup>. Many of these potential applications require the chemical modification of CNTs with specific functionalities<sup>[5-8]</sup>. It is believed that the fabrication of optically and electronically active composites of organic materials and CNTs will create new applications for nanotechnology and advanced nanodevices. Porphyrins are stable natural functional

dyes with a large extinction coefficient in the visible light region, have predictable rigid structures, and possess prospective photochemical electron-transfer ability, and extensively used in self-assembling processes to prepare monolayer and multilayer films which are of fundamental importance for study of energy and electron transfer between the light-harvesting antenna and the photosynthetic reaction centers<sup>[9-10]</sup>. The use of metalloporphyrins as catalysts in oxygenation reactions has been extensively investigated in biomimetic studies as well as in industrial applications<sup>[11]</sup>. In particular, there have been a number of reports on heterogeneous catalytic oxygenation sys-

收稿日期: 2010-05-27。收修改稿日期: 2010-07-07。

江苏省自然科学基金(No.BK2006717)资助项目。

\*通讯联系人。E-mail: yingui@nju.edu.cn, Tel: 025-83592529, Fax: 025-83314502

第一作者: 佟履冰, 女, 26 岁, 硕士研究生; 研究方向: 碳材料有机功能化。

tems, in which metalloporphyrin catalysts are immobilized on soluble or insoluble polymer supports such as surface-modified mesoporous silica, Merrifield's resins, and highly cross-linked polymers. CNTs can serve as electron acceptor components in donor-acceptors. Accordingly, a donor-acceptor system with porphyrin-CNT architectures involving covalent or noncovalent linkages has been studied<sup>[12-17]</sup>. Recently Garcia and co-workers have reported the interaction of zinc porphyrin with pyridyl functionalized SWCNTs through an apical coordinative bond between the porphyrin transition metal atom and the pyridyl ligand<sup>[18]</sup>. Yu et al. reported that ruthenium porphyrin functionalized single-walled carbon nanotube arrays have been prepared using coordination of the axial position of the metal ion onto 4-aminopyridine preassembled single-walled carbon nanotubes directly anchored to a silicon(100) surface (SWCNTs-Si)<sup>[19]</sup>. In this paper, we report functional multi-walled carbon nanotubes (MWCNTs) containing pyridyl groups to form a supramolecular system with zinc tetraphenylporphyrin via axial coordination.

## 1 Experimental

### 1.1 Materials

The MWCNTs (purity >95wt%, diameter about 8

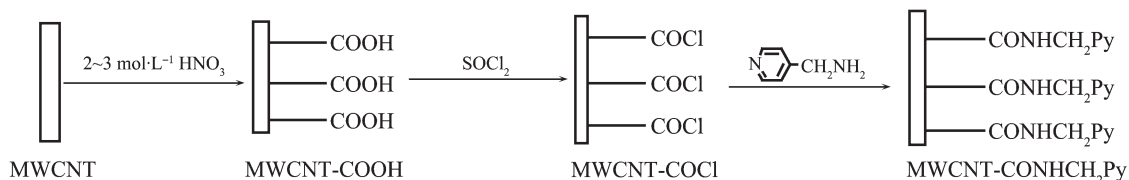
nm, length about 50  $\mu\text{m}$ ) were purchased from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. 4-aminomethylpyridine (PyCH<sub>2</sub>NH<sub>2</sub>, A.R.) and zinc tetraphenylporphyrin (ZnTPP, A.R.) were purchased from Aldrich. All solvents were A.R. grade and were purified before use.

### 1.2 Instruments

Raman spectrum was obtained on JY-HR 800 Raman spectrometer with an excited wavelength 488 nm. Transmission electron microscope (TEM) images were obtained on a JEM-200CX, JEOL, using an accelerating voltage of 200 kV. Fourier transform-infrared (FTIR) spectra were recorded on a Bruker Vector 22 spectrometer. UV-Vis absorption spectra were recorded on Shimadzu UV-3100. Fluorescence emission and excitation spectra were recorded on an Aminco Bowman Series 2 spectrofluorimeter equipped with a R928 photomultiplier working at 850 V and pass width is 4 nm. UV-Vis and fluorescence emission were determined at room temperature without degassed in a standard quartz cell with the path-length of 1 cm.

### 1.3 Synthesis

The synthesis of chemically modified MWCNT-CONHCH<sub>2</sub>Py was carried out as indicated in Scheme 1.



Scheme 1 Synthetic route for the preparation of MWCNT-CONHCH<sub>2</sub>Py

Carboxylic group-functionalized MWCNTs (MWCNT-COOH) were prepared by literature procedure<sup>[20-21]</sup>. The MWCNTs (100 mg) were refluxed in 100 mL of 3 mol·L<sup>-1</sup> nitric acid for 24 h to introduce carboxylic groups on the wall of MWCNTs. The MWCNT-COOH (40 mg) in 5 mL of SOCl<sub>2</sub> together with 3 drops of DMF were stirred at 80 °C for 24 h to give MWCNT-COCl<sup>[22]</sup>. The excess SOCl<sub>2</sub> was removed in vacuo and the dried MWCNT-COCl was gained. Then MWCNT-COCl (20 mg) and 4-aminomethylpyridine (150 mg) in pyridine (10 mL) were refluxed for 3 days. After cooling, the solid was repeatedly treated with

EtOH by sonicating and centrifuging procedure to remove free amine. The solid was dried in vacuo to gain MWCNT-CONHCH<sub>2</sub>Py.

The self-assembly of MWCNT-CONHCH<sub>2</sub>Py and ZnTPP was performed as follows: 20 mg MWCNT-CONHCH<sub>2</sub>Py were added to 2×10<sup>-5</sup> mol·L<sup>-1</sup> solution of ZnTPP in CHCl<sub>3</sub> (15 mL), and then sonicated for 2 h at room temperature, followed by low speed centrifugation of the suspension to remove insoluble nanotubes (1 000 r·min<sup>-1</sup>), and further high speed centrifugation to remove soluble ZnTPP (10 000 r·min<sup>-1</sup>). The solid materials were dried in a dinitrogen atmosphere to get self-

assembly of MWCNT-CONHCH<sub>2</sub>Py-ZnTPP composite.

## 2 Results and discussion

### 2.1 Characterization

#### 2.1.1 FTIR spectra

Although the infrared spectra of pristine MWCNTs are featureless, FTIR spectroscopy is very informative for studying the functional groups attached to the MWCNTs walls.

Fig.1 shows FTIR spectra of MWCNTs, MWCNT-COOH, MWCNT-CONHCH<sub>2</sub>Py and 4-aminomethylpyridine. Compared with MWCNTs, the broad peak of MWCNT-COOH in the 3 100~3 600 cm<sup>-1</sup> region is characteristic of O-H. The band at 1 718 cm<sup>-1</sup> can be identified as the carbonyl stretching mode. The MWCNT-CONHCH<sub>2</sub>Py has the characteristic *sp*<sup>3</sup>  $\nu_{C-H}$  stretching signals between 2 800~3 000 cm<sup>-1</sup>, the  $\nu_{C-H}$  bending signal of N-CH<sub>2</sub> at 1 406 cm<sup>-1</sup>, and the peaks at 812, 1 270 and 1 596 cm<sup>-1</sup> from 4-aminomethylpyridine. There is a small new peak at 1 658 cm<sup>-1</sup>, which can be ascribed to the C=O stretch mode of amide carbonyl group<sup>[23]</sup>. These confirm that MWCNTs were modified by 4-aminomethylpyridine. In addition, the peak at 1 718 cm<sup>-1</sup> still exists in the IR spectrum of MWCNT-CONHCH<sub>2</sub>Py, which indicates that there are unreacted carboxyl acid groups on side wall of MWCNTs.

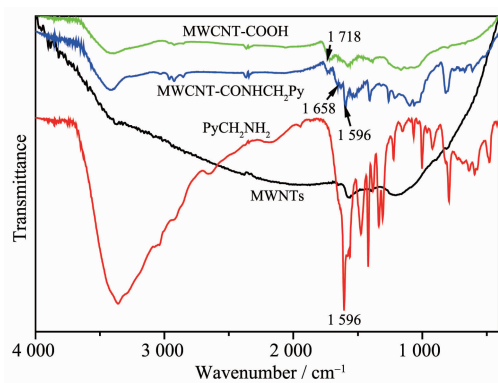


Fig.1 FTIR spectra of MWCNTs, MWCNT-COOH, MWCNT-CONHCH<sub>2</sub>Py and PyCH<sub>2</sub>NH<sub>2</sub>

#### 2.1.2 Raman spectra

Raman spectroscopy has been used widely for characterization of carbon nanotubes.

Fig.2 is the Raman spectra of MWCNT-CONHCH<sub>2</sub>Py and the raw MWCNT, and both of them

show a band at about 1 575 cm<sup>-1</sup> (G band), which is the characteristic tangential-mode of graphic and a disorder-induced peak at 1 356 cm<sup>-1</sup> (D band). Furthermore a new peak emerges around 1 605 cm<sup>-1</sup> assigned as the D band<sup>[24]</sup>. The D band from *sp*<sup>3</sup> carbon including out-layer and inner-layer of the MWCNT wall<sup>[25-26]</sup>, but the relative intensity of D band and G band changes a lot. The change of the intensity of D band relative to G band provides a diagnostic indicator of the new formation of *sp*<sup>3</sup> C atoms in the surface of the nanotubes wall due to HNO<sub>3</sub> treatment, suggesting the new covalent bonds forming in MWCNTs-CONHCH<sub>2</sub>Py<sup>[27-28]</sup>. It is the reason that the D-band is stronger in the MWCNTs-CONHCH<sub>2</sub>Py than in the pristine MWCNTs.

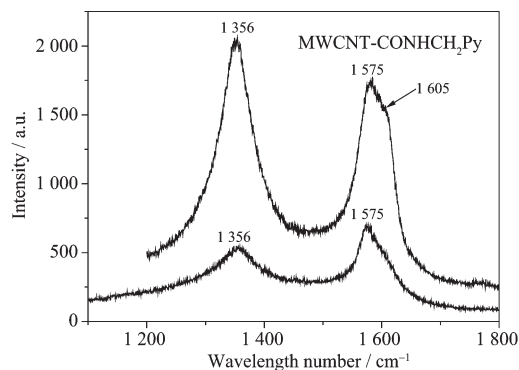


Fig.2 Raman spectra of MWCNT-CONHCH<sub>2</sub>Py and pristine MWCNT

### 2.2 Supramolecule MWCNT-CONHCH<sub>2</sub>Py-ZnTPP

#### 2.2.1 TEM

Fig.3 showed TEM images of MWCNTs, MWCNT-CONHCH<sub>2</sub>Py and MWCNT-CONHCH<sub>2</sub>Py-ZnTPP. Due to the length of the pristine MWCNTs is quite long, (Fig.3a) which means that the most part of the pyridyl groups are attached on the side wall, and the pyridyl groups on the tube-ends, compared to one on the side wall, are only a small part. Compared with Fig.3a, the morphology of MWCNT-CONHCH<sub>2</sub>Py in Fig.3b only has a few changes because the attached group is not bulk enough, while the morphology of the MWCNT-CONHCH<sub>2</sub>Py-ZnTPP in Fig.3c changes a lot. The thickness of the carbon nanotubes increases remarkably, which shows that there have some soft materials attached on the wall of the carbon nanotubes.

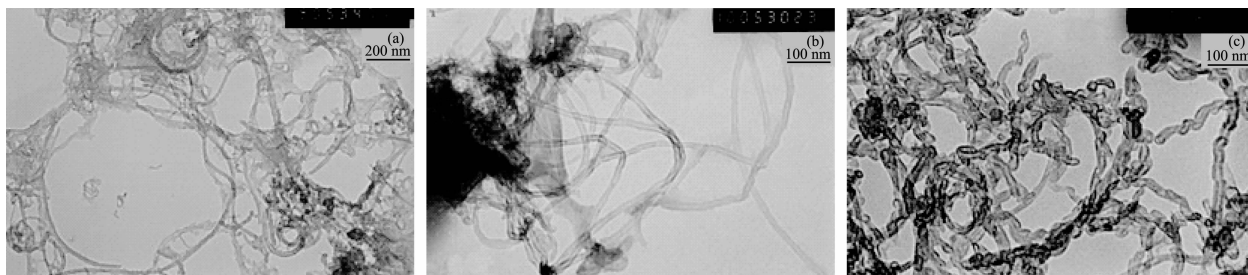


Fig.3 TEM images: (3a) MWCNT; (3b) MWCNT-CONHCH<sub>2</sub>Py and (3c) MWCNT-CONHCH<sub>2</sub>Py-ZnTPP

### 2.2.2 UV-Vis spectra and Fluorescence spectra

The formation of axial coordination complex of MWCNT-CONHCH<sub>2</sub>Py and ZnTPP can be diagnosed by UV-Vis spectrum<sup>[29-30]</sup>.

Fig.4a showed UV-Vis absorption spectra of ZnTPP and MWCNT-CONHCH<sub>2</sub>Py-ZnTPP in CHCl<sub>3</sub> (1  $\mu\text{mol} \cdot \text{L}^{-1}$ ) at room temperature. The UV-Vis spectra showed that the addition of MWCNTs-CONHCH<sub>2</sub>Py to a solution of ZnTPP in CHCl<sub>3</sub> resulted in spectral changes characteristic of the presence of pentacoordinated ZnTPP. The Soret and Q bands of compound ZnTPP were red-shifted as shown in Fig.4a. This behavior follows the trend of what has been observed for the fullerene analogue, but the changes observed for MWCNTs-CONHCH<sub>2</sub>Py are less pronounced. The results indicated that: (i) the formation of shoulder peaks

suggests that only part of ZnTPP formed axial coordination complex with MWCNT-CONHCH<sub>2</sub>Py; (ii) another part of ZnTPP attached onto sidewall of MWCNTs by  $\pi$ - $\pi$  and van der Waals interactions which does not cause spectral shift<sup>[31]</sup>. Fig.4b showed the room temperature fluorescence spectrum of ZnTPP, MWCNT-COOH-ZnTPP and MWCNTs-CONHCH<sub>2</sub>Py-ZnTPP in CHCl<sub>3</sub>. The absorbance of samples was tuned into 0.7 a.u. at the excitation wavelength. The fluorescence quantum yield from the ZnTPP part decreased to 40%, 15% of that of ZnTPP when added MWNT-COOH and MWCNTs-CONHCH<sub>2</sub>Py, respectively. The reduced fluorescence quantum yield of the ZnTPP attached to MWCNTs via  $\pi$ - $\pi$  interaction and axial coordination interaction may be attributed to energy transfer or electron transfer from ZnTPP to MWCNTs.

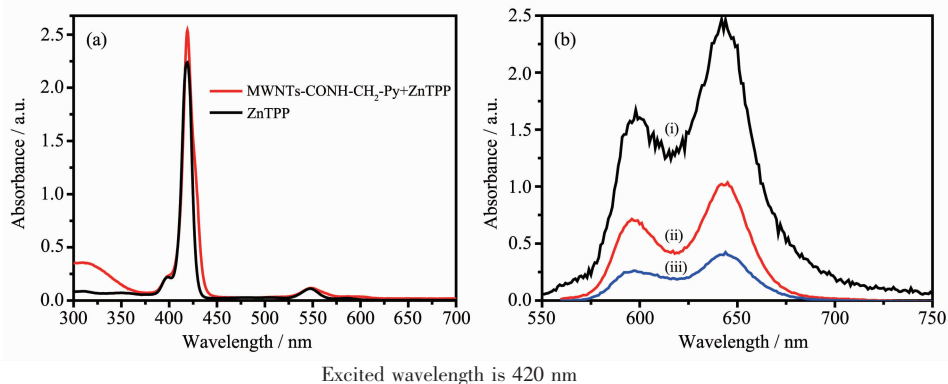


Fig.4 (a) UV-Vis spectra of ZnTPP and MWCNT-CONHCH<sub>2</sub>Py-ZnTPP in CHCl<sub>3</sub>; (b) Fluorescence spectra of ZnTPP (i), MWCNT-COOH-ZnTPP (ii), and MWCNT-CONHCH<sub>2</sub>Py-ZnTPP (iii) in CHCl<sub>3</sub>

## 3 Conclusion

We prepared functional multi-walled carbon nanotubes (MWCNTs) containing pyridyl group. The UV-Vis and fluorescence spectrum and TEM demonstrated the formation of an axial coordination supramolecular MWCNT-CONHCH<sub>2</sub>Py-ZnTPP. MWCNTs can effectively quench fluorescence of ZnTPP via

axial coordination.

## References:

- [1] Iijima S. *Nature*, **1991**, *354*:56-58
- [2] Khabashesku V N, Billups W E, Margrave J L. *Acc. Chem. Res.*, **2002**, *35*:1087-1095
- [3] MI Hong-Yu(米红宇), ZHANG Xiao-Gang(张校刚), LÜ Xin-

- Mei(吕新美), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2007**,**23**(1):159-163
- [4] LI Ke(李克), LÜ Gong-Xuan(吕功煊), LIU Jian-Fu(刘建福). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2005**,**21**(10): 1571-1575
- [5] Sun Y P, Fu K, Lin Y, Huang W J. *Acc. Chem. Res.*, **2002**,**35**: 1096-1104
- [6] Qiu J, Zhang Sh H, Wang G J, et al. *New Carbon. Mater.*, **2009**,**24**:344-348
- [7] LI Hao-Peng(李浩鹏), ZHANG Xiao-Yan(张晓艳), CUI Xiao-Li(崔晓莉). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2009**,**25**(11):1935-1938
- [8] TANG Ya-Wen(唐亚文), CAO Shuang(曹爽), CHEN Yu(陈煜), et al. *Chem. J. Chinese Universities. (Gaodeng Xuexiao Huaxue Xuebao)*, **2007**,**28**(5):936-939
- [9] Wojaczynski L, Latos-Grazynski L. *Coordin. Chem. Rev.*, **2000**,**204**:113-171
- [10] Gust D, Moore T A. *Top. Curr. Chem.*, **1991**,**159**:103-151
- [11] Choi B G, Song R, Nam W, et al. *Chem. Commun.*, **2005**: 2960-2962
- [12] Guldi D M, Prato M. *Chem. Commun.*, **2004**:2517-2525
- [13] Baskaran D, Mays J, Zhang X P, et al. *J. Am. Chem. Soc.*, **2005**,**127**:6916-6917
- [14] Hasobe T, Fukuzumi S, Kamat P V. *J. Am. Chem. Soc.*, **2005**, **127**:11884-11885
- [15] Li H, Martin R B, Harruff B A, et al. *Adv. Mater.*, **2004**,**16**: 896-900
- [16] Murakami H, Nomura T, Nakashima N. *Chem. Phys. Lett.*, **2003**,**378**:481-485
- [17] Guldi D M, Ramey J, Marcaccio M, et al. *Chem. Commun.*, **2004**:2034-2035
- [18] Alvaro M, Atienzar P, la Cruz P, et al. *J. Am. Chem. Soc.*, **2006**,**128**:6626-6635
- [19] Yu J X, Mathew S, Flavel B S, et al. *J. Am. Chem. Soc.*, **2008**, 130:8788-8796
- [20] Flahaut E, Bacsá R, Peigney A, et al. *Chem. Commun.*, **2003**: 1442-1443
- [21] Liu J, Rinzler A G, Dai H, et al. *Science*, **1998**,**280**:1253-1256
- [22] Hu H, Bhowmik P, Zhao B, et al. *Chem. Phys. Lett.*, **2001**, **345**:25-28
- [23] Peng H, Alemany L B, Margrave J L, et al. *J. Am. Chem. Soc.*, **2003**,**125**:15174-15182
- [24] Bacsá W S, Ugrate D, Chatelain A, et al. *Phys. Rev.*, **1994**, **B50**:15473-15476
- [25] Deng Y H, Deng C H, Yang D, et al. *Chem. Commun.*, **2005**: 5548-5550
- [26] Hamon M A, Chen J, Hu H, et al. *Adv. Mater.*, **1999**,**11**:834-840
- [27] Dyke C A, Tour J M. *J. Am. Chem. Soc.*, **2003**,**125**:1156-1157
- [28] Pan H L, Liu L Q, Guo Z X, et al. *Nano Lett.*, **2003**,**3**:29-32
- [29] El-Khouly M E, Ito O, Smith P M, et al. *Photochem. Photobio. C: Photochem. Rev.*, **2004**,**5**:79-104
- [30] Guldi D M, Luo C, Da Ros T, et al. *Chem. Commun.*, **2000**: 375-376
- [31] Li H, Zhou B, Lin Y, et al. *J. Am. Chem. Soc.*, **2004**,**126**: 1014-1015