Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Complex of Porphyrins and Cyclodextrin-modified Multi-walled Carbon Nanotubes: Preparation and its Properties

L. Zhang[a]; X. Li[a]; S. -Z. Kang[a]; J. Mu[a]
[a] Department of Chemistry, Key Laboratory for Ultrafine Materials of Ministry of Education, East China University of Science and Technology, Shanghai, P. R. China

To cite this Article Zhang, L. , Li, X. , Kang, S. -Z. and Mu, J.(2008) 'Complex of Porphyrins and Cyclodextrin-modified Multi-walled Carbon Nanotubes: Preparation and its Properties', Supramolecular Chemistry, 20: 6, 601 — 604
To link to this Article: DOI: 10.1080/10610270701543423
URL: http://dx.doi.org/10.1080/10610270701543423

Supramolecular Chemistry, September 2008 VOL. 20 (6), pp. 601–604

Complex of Porphyrins and Cyclodextrin-modified Multi-walled Carbon Nanotubes: Preparation and its Properties

L. ZHANG, X. LI, S. -Z. KANG and J. MU*

Department of Chemistry, Key Laboratory for Ultrafine Materials of Ministry of Education, East China University of Science and Technology, Shanghai, P. R. China

(Received 9 April 2007; Accepted 28 June 2007)

A complex (C1) of tetrakis(4-hydroxylphenyl)porphyrin (THPP) and cyclodextrin-modified multi-walled carbon nanotubes (MWNTs-CD) was prepared. The UV-vis spectra show that the absorption bands of C1 are almost the same as those of THPP, implying that the electron distribution of THPP is not influenced by MWNTs-CD. On the other hand, the fluorescence of THPP is quenched, suggesting that there exists energy transfer between THPP and MWNTs-CD. In order to understand the interaction between THPP and MWNTs-CD, the electrochemical behavior of C1 was explored with cyclic voltammetry. The results display that the electrochemical behavior of C1 is similar to that of the inclusion complex of amino-modified cyclodextrin and THPP, but different from that of the MWNTs-CD. These phenomena indicate that the cyclodextrin moieties play an important role in the interaction between THPP and MWNTs-CD.

Keywords: Porphyrin; Carbon nanotube; Cyclodextrin; Inclusion complex

INTRODUCTION

It is well-known that fullerenes and carbon nanotubes are excellent assembly units for the development of optoelectronic and photovoltaic devices due to their novel electronic properties [1,2]. In recent years, a great deal of attention has been paid to the photophysical properties of derivatives of carbon nanotubes and fullerenes via a noncovalent or covalent linkage, for the sake of photoresponsive materials [3,4]. Therein, the complexes of porphyrins and carbon nanotubes have been explored. For example, porphyrins have been introduced to the surface of carbon nanotubes through electrostatic interaction [5], $\pi-\pi$ interaction [6], axial coordination [7], and so on. In these systems, when excited at an appropriate wavelength of light, the porphyrins can act as an energy/electron donor substructure meanwhile the carbon nanotubes act as the corresponding acceptor moiety. Recently, some of these systems have been used to construct photovoltaic cells [8,9].

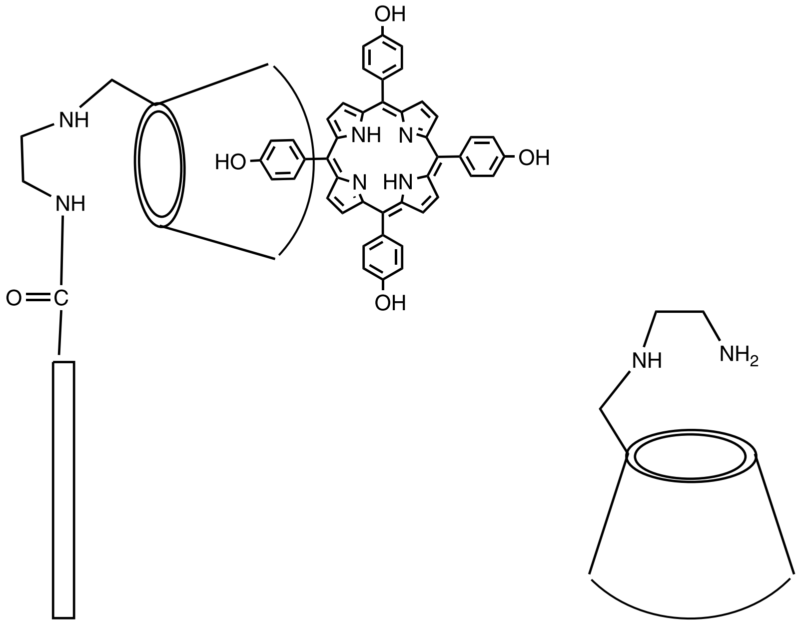
Considering the excellent performance in promoting electron transfer, carbon nanotubes appear to be an important candidate in the fabrication of nanocircuits. It is known that cyclodextrins (CDs) can selectively bind various organic, inorganic and biological molecules into their cavities to form supramolecular complexes in aqueous solutions [10]. If carbon nanotubes are modified with cyclodextrins, it is possible to add some selective assembling sites on the carbon nanotubes, which is very encouraging for the fabrication of combinational nano-devices. However, to our best knowledge, there are few reports on the complexes of cyclodextrin-modified multi-walled carbon nanotubes and functional molecules.

In the present work, the cyclodextrin-modified multi-walled carbon nanotubes (MWNTs-CD) and the tetrakis(4-hydroxylphenyl)porphyrin (THPP) were chosen as a model system. The complex (C1) of MWNTs-CD and THPP was formed via simple mixing, and the optical properties were characterized with UV-vis spectra and fluorescence spectra. Furthermore, the electrochemical behavior of C1 was also explored with cyclic voltammetry.

---

*Corresponding author. E-mail: jinmu@ecust.edu.cn

ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270701543423



C1 CD-NH$_2$

SCHEME 1 Structures of C1 and CD-NH$_2$.

EXPERIMENTAL

Materials

THPP was prepared and purified according to the method in ref. [11]. MWNTs and MWNTs possessing carboxylic group (MWNTs-COOH) were prepared by the methods similar to those reported previously [12,13]. MWNTs-CD was prepared according to ref. [14]. Other reagents were obtained from commercial sources and used as received.

Preparation of C1

MWNTs-CD was added into a 20 mL DMF solution of THPP (8.75×10^{-6} mol·L^{-1}). The mixture was stirred for 2 h at room temperature, then filtered and washed with DMF and water, respectively. The target product, C1, was obtained after drying overnight at 60°C. The structure of C1 is shown in Scheme 1.

Measurements

UV-vis spectra were measured with UV-2102 UV-vis spectrophotometer (Unico). Fluorescence spectra were recorded with RF-5301PC spectrophotometer (Shimadzu). Cyclic voltammograms were obtained on PCI 4/300 electrochemical system (GAMRY Instruments) in a standard three-electrode cell consisting of a glass carbon electrode (GCE) as the working electrode (polished with 0.3 μm aluminum paste and ultrasonicated in deionized water and DMF, respectively), a platinum electrode as the counter electrode, and an Ag/AgCl electrode as the reference electrode. After bubbling N$_2$ into the system for 30 min, the voltammetry was performed at a rate of 100 mV·s^{-1} in the supporting electrolyte solution of tetra-n-butylammonium perchlorate (0.1 mol·L^{-1} in DMF). Experiments were performed at 27 ± 1°C.

RESULTS AND DISCUSSION

UV-vis Spectra of C1

UV-vis spectra of C1 with various concentrations of MWNTs-CD are shown in Fig. 1. It can be seen that there is one Soret band at 422 nm and four Q bands at 519, 556, 596, and 653 nm for C1. Compared with the UV-vis spectrum of THPP, the absorption bands of C1 do not shift with increasing MWNTs-CD concentrations. The result shows that the electron distribution of THPP is not influenced by MWNTs-CD. Our experimental results reported previously [15] show that the electron transfer can take place when the organic molecules interact with the tubular fragment of carbon nanotubes. Therefore, it can be deduced that the THPP molecules are included into the cavities of cyclodextrins, as shown in Scheme 1, while no interaction with the tubular fragment of carbon nanotubes takes place. In order to further confirm that the THPP molecules are included into

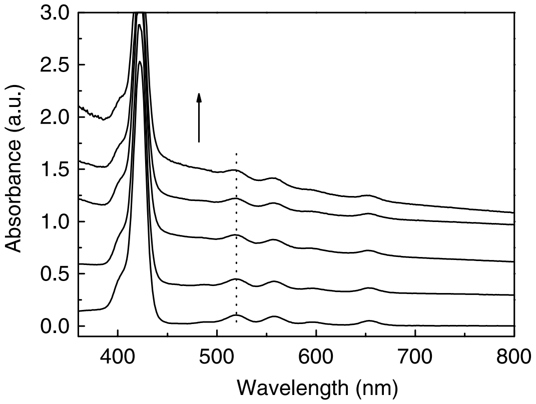


FIGURE 1 UV-vis spectra of solutions of THPP (8.75×10^{-6} mol·L^{-1} in DMF) with increasing concentrations of MWNTs-CD. The arrow indicates the increasing direction of MWNTs-CD concentrations, which are 0, 0.02, 0.05, 0.07, 0.10 mg·mL^{-1}, respectively.

the cavities of cyclodextrins, the apparent stability constant (Kα) of the inclusion complex of THPP and amino-modified cyclodextrin (CD-NH_2) was measured by spectra titration. The stoichiometric ratio of THPP to CD-NH_2 was determined by the molar ratio method, before the Kα was calculated [16]. The stoichiometric ratio of THPP to CD-NH_2 in the complex is 1:1. And $K\alpha = 3.48 \times 10^5$. The results show that there exists a relatively strong interaction between cyclodextrin and THPP. Therefore it is reasonable to deduce that the THPP molecules are included into the cavities of cyclodextrins as the previous reports [17–19].

Fluorescence Spectra of C1

Figure 2A shows the fluorescence spectra of C1 with various concentrations of MWNTs-CD. As can be seen from Fig. 2A, there exist two emission bands at 660 nm and 724 nm for C1. The emission of organic molecules is usually enhanced when they are included in the cavities of cyclodextrins. It is interesting that the fluorescence is quenched due to introduction of MWNTs-CD, compared with that of THPP. Moreover, along with increasing concentrations of MWNTs-CD, the fluorescence intensity is weakened gradually. Combined with that of UV-vis spectra of C1, it can be deduced that there exists energy transfer between THPP and MWNTs-CD. The similar phenomenon is observed when the small organic molecules are included in the cavities of cyclodextrin moieties on the MWNTs-CD [14]. Thus the cyclodextrin moieties on the MWNTs-CD provide the host sites with a microenvironment which is essential for the energy transfer between functional molecules and MWNTs-CD. These results imply that it is possible to integrate some functional blocks on the carbon nanotubes and to fabricate the energy channel among these blocks by using of MWNTs-CD.

Figure 2B shows the relationship between the relative emission intensity (I_0/I) at 660 nm and the concentration of MWNTs-CD. I_0 and I refer to the fluorescence intensity of THPP and C1, respectively. A good linearity of I_0/I versus the concentration of MWNTs-CD is obtained, implying that it is limited by one THPP molecule being simultaneously included in several cyclodextrin moieties. This result further indicates that the presumed structure shown in Scheme 1 is reasonable.

Electrochemical Behavior of C1

Figure 3 shows cyclic voltammograms of MWNTs-CD, inclusion complex of CD-NH_2 and THPP, and C1. The CV of MWNTs-CD displays two reduction peaks at −0.76 V and −1.46 V, and three oxidation peaks at −1.17 V, −0.05 V and +1.19 V, respectively. The CV of the complex of THPP and CDs-NH_2 shows

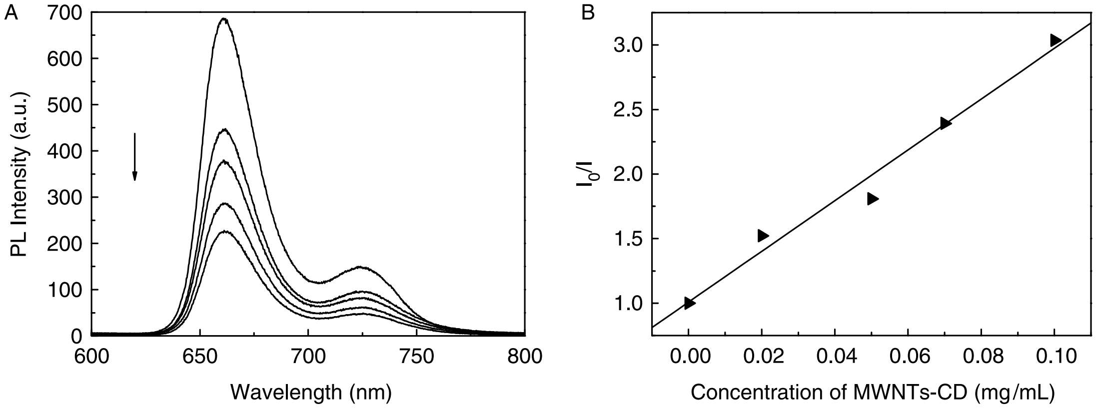


FIGURE 2 (A) Fluorescence spectra of THPP in DMF (8.75×10^{-6} mol·L^{-1}) upon increasing concentrations of MWNTs-CD ($\lambda_{ex} = 560$ nm). The arrow indicates the increasing direction of MWNTs-CD concentrations, which are 0, 0.02, 0.05, 0.07, 0.10 mg·mL^{-1}, respectively. (B) Plot of relative emission intensity at 660 nm versus concentration of MWNTs-CD.

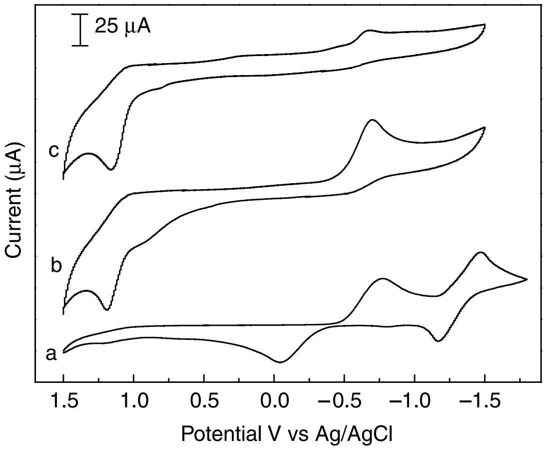


FIGURE 3 Comparative CVs of MWNTs-CD (a), inclusion complex of CD-NH_2 and THPP (b), and C1 (c). The concentration of THPP in (b) and (c) is 8.75×10^{-6} mol·L^{-1}. The molar ratio of CDs to THPP in (b) and (c) is 1:2.

one reduction peak at −0.69 V and two oxidation peaks at −0.60 V and +1.19 V, respectively. Being similar to the CV of the complex of THPP and CD-NH_2, the CV of C1 displays one reduction peak at −0.66 V and two oxidation peaks at −0.55 V and 1.16 V, respectively. For the redox peaks of C1 (−0.69 V, −0.60 V) and the complex of THPP and CD-NH_2 (−0.66 V, −0.55 V), the control experiment (not shown here) shows that they may be ascribed to the redox of THPP. Also it can be found that the redox couple of THPP is more positive than that of MWNTs-CD. Therefore, the presence of THPP in C1 may restrain the electron transfer between MWNTs and the electrode. These results indicate that the microenvironment around the THPP molecules in C1 is similar to that in the complex of THPP and CD-NH_2. Therefore, it is further demonstrated that THPP molecules are included in the cavities of cyclodextrins, while no interaction exists with the tubular fragment of carbon nanotubes.

CONCLUSIONS

The complex of THPP and cyclodextrin-modified multi-walled carbon nanotubes was prepared. The THPP molecules are included in the cavities of cyclodextrins, while there is no interaction with the tubular fragment of carbon nanotubes. There exists energy transfer between THPP and MWNTs-CD. The cyclodextrin moieties on the MWNTs-CD provide the guest molecules with the microenvironment that is essential for energy transfer.

References

[1] Banerjee, S.; Kahn, M. G. C.; Wong, S. S. *Chem. Eur. J.* **2003**, *9*, 1898.
[2] Dyke, C. A.; Tour, J. M. *Chem. Eur. J.* **2004**, *10*, 812.
[3] Freitag, M.; Martin, Y.; Misewich, J. A.; Martel, R.; Avouris, P. *Nano Lett.* **2003**, *3*, 1067.
[4] Cao, L.; Chen, H.; Wang, M.; Sun, J.; Zhang, X.; Kong, F. *J. Phys. Chem. B* **2002**, *106*, 8971.
[5] Chen, J.; Collier, C. P. *J. Phys. Chem. B* **2001**, *109*, 7605.
[6] Hasobe, T.; Hattori, S.; Kamat, P. V.; Fukuzumi, S. *Tetrahedron* **2006**, *62*, 1937.
[7] Alvaro, M.; Atienzar, P.; De la Cruz, P.; Delgado, J. L.; Troiani, V.; Garcia, H.; Langa, F.; Palkar, A.; Echegoyen, L. *J. Am. Chem. Soc.* **2006**, *128*, 6626.
[8] Imahori, H.; Fukuzumi, S. *Adv. Funct. Mater.* **2004**, *14*, 525.
[9] Hasobe, T.; Kashiwagi, Y.; Absalom, M. A.; Sly, J.; Hosomizu, K.; Crossley, M. J.; Imahori, H.; Kamat, P. V.; Fukuzumi, S. *Adv. Mater.* **2004**, *16*, 975.
[10] Liu, Y.; Kang, S.; Zhang, H. *Microchem. J.* **2001**, *70*, 115.
[11] Adler, A. D.; Longo, F. R.; Kampas, F. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
[12] Journet, C.; Maser, W. K.; Bernier, P.; Loisenu, A.; Lamy de la Chapple, M.; Lefrant, S.; Deniard, P.; Lee, R.; Ficher, J. E. *Nature* **1997**, *338*, 756.
[13] Banerjee, S.; Hemraj-Benny, T.; Wong, S. S. *Adv. Mater.* **2005**, *17*, 17.
[14] Kang, S.; Cui, Z.; Liu, L.; Mu, J. *Fullerene. Nanot. Carbon Nanostruct.* **2005**, *13*, 353.
[15] Kang, S.; Cui, Z.; Liu, L.; Mu, J. *J. Disper. Sci. Technol.* **2006**, *27*, 45.
[16] Tawarah, K. M.; Khouri, S. J. *Dyes Pigments* **2000**, *45*, 229.
[17] Kong, L. -H.; Guo, Y. -J.; Li, X. -X.; Pan, J. -H. *Spectrochim. Acta Part A* **2007**, *66*, 594.
[18] Lang, K.; Kral, V.; Kapusta, P.; Kubatd, P.; Vasekb, P. *Tetrahedron Lett.* **2002**, *43*, 4919.
[19] French, R. R.; Holzer, P.; Leuenberger, M.; Nold, M. C.; Woggon, W. *J. Inorg. Biochem.* **2002**, *88*, 295.