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Light-harvesting dendrimer zinc-phthalocyanines chromophores labeled single-wall carbon nanotube nanoensembles: Synthesis and photoinduced electron transfer

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ABSTRACT

A novel series of light-harvesting dendrimer zinc-phthalocyanines chromophores labeled-single-wall carbon nanotubes (SWNTs) nanoparticles, in which 0–2 generations dendrimer zinc phthalocyanines covalently linked with SWNTs using either ethylenediamine or hexamethylenediamine as the space linkers were prepared. The structures and morphologies of these nanoconjugates were comprehensively characterized by Raman spectroscopy, transmission electron microscopy and thermal gravimetric analysis methods. Their photophysical properties were investigated by fluorescence and time-resolved spectroscopic methods. The photoinduced intramolecular electron transfer occurred from phthalocyanines (donors) to SWNTs (acceptors). Besides, the electron transfer exchange rates and exchange efficacies between the dendritic phthalocyanines and single-wall carbon nanotubes increased as the length of spacer linker decreased, or as the dendritic generation increased. Cyclic voltammetry (CV) method further confirmed thermodynamics possibility of the electron transfer from phthalocyanines to single-wall carbon nanotubes. These new nanoconjugates are fundamentally important due to the synergy effects of both carbon nanotubes and dendrimer phthalocyanines, which may find potential applications in the fields of drug delivery, biological labeling, or others.

1. Introduction

Nanotechnology has emerged as a major subject in contemporary research, which is of high technological significance and interest to many researchers [1]. Carbon-based nanomaterials have attracted numerous attentions on production of innovative materials, composites and electronic devices because of their small dimensions. In particular, the extended π-electron systems of single-wall carbon nanotubes (SWNTs) are considered as highly promising carbon-based nanomaterials. Their unique structure, electronic conductivity, optical properties and high chemical stability make them ideal nanomaterials for applications in many areas, such as sensing, photoelectronic devices, various photo-harvesting and biological applications [2]. More recently, incorporation of light-harvesting antenna molecules, such as dendrimers that are able to absorb light and channel it to a reaction core into the extended π electrons of carbon nanotubes, would constitute an ideal supra-molecular nanoassemble which can realized intramolecular electron transfer processes upon photo-excitation [3,4]. The dendrimers employed are generally poly (amidoamine) dendrimers or dendrons (PAMAM) [5–8], poly (propyleneimine) dendrimers (PPI) [9], polyphenylene dendrimers, dendrimer prophyrins and dendrimer phthalocyanines [10–20].

Dendrimer phthalocyanines, a phthalocyanine chromophore encapsulated within the inner core of dendrimers with surface functionalized groups, were considered as a new efficient light-harvesting system. They possess a structure with a high density of a limited number of functional groups on the phthalocyanine ring [21]. Hahn group immobilized water-soluble dendritic phthalocyanines with ethylene glycol monomethyl ether terminal groups on SWNTs [22]. In our previous study, the first generation of dendrimer zinc phthalocyanines functionalized single-wall carbon nanotubes nanoconjugates was synthesized. The effect of the length of spacer linker on the photoinduced electron transfer was also studied [23].

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In this study, we synthesized and characterized a series of nanoconjugates, in which 0–2 generations of dendrimer zinc phthalocyanines chromophores were functionalized on SWNTs using either ethylenediamine or hexamethylenediamine as spacer linker. The photophysical properties and photoinduced electron transfer properties of these dendrimer phthalocyanine-SWNTs nanoconjugates were studied by fluorescence and UV/vis spectroscopic methods. The effect of dendritic generations on the photoinduced electron transfer as well as electrochemical behaviors of nanoconjugates was.

2. Experimental

2.1. Materials and methods

Solvents for organic synthesis were reagent grade, and dried according to standard procedures. All other compounds were used as received. SWNTs-COOH has a diameter of 1–2 nm with a length of 5–30 μm, and a purity $>90\%$.

IR spectra were measured on Perkin Elmer IR spectrometers. Raman spectra were measured at room temperature with a Renishaw micro-Raman spectroscopic system (Renishaw Invia, UK) and a diode laser operating at a wavelength of 785 nm as an excitation source. The UV/vis spectra were recorded on a Cary 50 UV/vis spectrophotometer. Fluorescence spectra were carried out on an FL 900/FS 920 fluorescence spectrophotometer. Thermal properties of the nanoconjugates were measured using a Mettler-Toledo TGA/SDTA851e analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. Transmission electron microscopy (TEM) images were recorded on a JEM-2010 transmission electron microscope at 200 kV accelerating voltage. The cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements were carried out on a CHI660D electrochemical workstation utilizing a three-electrode configuration at 25 °C. A bare carbon paste electrode (CPE) served as working electrode and a Pt wire as counter electrode. A saturated Ag/AgCl electrode was employed as the reference electrode. Electrochemical grade TBAP in DMF (0.20 mol/L) was employed as the supporting electrolyte.

2.2. Synthesis

Dethylalcohol functionalized SWNTs (**SWNTs-E**), ethylalcohol functionalized SWNTs (**SWNTs-H)**, tetra-[3,5-di-(4-cyanobenzyloxy) benzyloxy] zinc(II) phthalocyanine dethylalcohol functionalized SWNTs (**SWNTs-H-8DZnPc**), and tetra-[3,5-di-(4-cyanobenzyloxy) benzyloxy]zinc(II) phthalocyanine dethylalcohol functionalized SWNTs (**SWNTs-E-8DZnPc**) and dendrimer phthalocyanines including tetra-carboxylic zinc (II) phthalocyanine (**4ZnPc**), tetra-[3,5-di(4-cyanobenzyloxy) benzyloxy] zinc (II) phthalocyanine (**8DZnPc**), and tetra-{3,5-di-[3,5-di-(4-cyanobenzyloxy) benzyloxy] benzyloxy} zinc (II) phthalocyanine (**16DZnPc**) also were synthesized according to the our group reported [24].

2.3. Synthesis of SWNTs-E-4ZnPc and SWNTs-H-4ZnPc

1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) (100 mg), 1-hydroxybenzotriazole (HOBT) (100 mg) and **4ZnPc** (20 mg) were added to a suspension of **SWNTs-E** (10 mg) in dry DMF (20 mL). The reaction mixture was continuously stirred at room temperature under nitrogen for 36 h. The solution was filtered and the black solid was washed with CH_2Cl_2, and dry by ethanol affording functionalized **SWNTs-E-4ZnPc**.

According to the above procedure, **SWNTs-H-4ZnPc** was prepared using **SWNTs-H** (10 mg) instead of **SWNTs-E.**

2.4. Synthesis of SWNTs-E-8DZnPc and SWNTs-H-8DZnPc

SWNTs-E-8DZnPc and **SWNTs-H-8DZnPc** were synthesized as we previously reported [24].

2.5. Synthesis of SWNTs-E-16DZnPc and SWNTs-H-16DZnPc

EDC·HCl (100 mg), HOBT (100 mg), and the dendritic phthalocyanine **16DZnPc** (20 mg) were added to a suspension of **SWNTs-E** (10 mg) in dry DMF (20 mL). The reaction mixture was continuously stirred at room temperature under nitrogen for 36 h. The solution was filtered, the black solid obtained was washed with CH_2Cl_2 and alcohol to afford **SWNTs-E-16DZnPc**.

According to the above procedure, **SWNTs-H-16DZnPc** was prepared using **SWNTs-H** (10 mg) instead of **SWNTs-E.**

3. Results and discussion

3.1. Characterization of nanoparticles

The synthetic scheme of 0–3 generations dendritic phthalocyanines chromophores covalently functionalized single-walled carbon nanotubes nanomaterial using either ethylenediamine or hexamethylenediamine as the spacer linkers was shown in Fig. 1. The structures of dendrimer phthalocyanines were unambiguously characterized by elemental analysis, MALDI-TOF-MS and ^{1}H NMR (See Supporting materials Figs. S1–S6). **SWNTs-E-4ZnPc** was obtained through the coupling reaction between the amine groups of **SWNTs-E/SWNTs-H** and the carboxylic groups of **4ZnPc** in the presence of EDC·HCl and HOBT. The similar reaction procedure leads to the other samples **SWNTs-H-4ZnPc**, **SWNTs-E-8DZnPc**, **SWNTs-H-8DZnPc**, **SWNTs-E-16DZnPc** and **SWNTs-H-16DZnPc**.

The structures and morphologies of the dendrimer phthalocyanine-functionalized SWNTs nanoconjugates (**SWNTs-E-4ZnPc**, **SWNTs-H-4ZnPc**, **SWNTs-E-8DZnPc**, **SWNTs-H-8DZnPc**, **SWNTs-E-16DZnPc** and **SWNTs-H-16DZnPc**) were fully characterized by TEM, IR and Raman spectroscopic methods. The amounts of dendrimer phthalocyanines covalently linked on the SWNTs were calculated by TGA method. The photophysical properties of the nanomaterials were also studied by UV/Vis, steady-state and time-resolved fluorescence spectroscopic methods.

The morphological structural characteristics of the nanoconjugates were studied by TEM. TEM images of dendrimer phthalocyanine-functionalized SWNTs nanoconjugates were shown in Fig. 2 and Fig. S7. Fig. 2(a) showed the clean sidewalls of the raw SWNTs with a diameter about 20 nm. The black spots originated from the dendrimer phthalocyanines on the SWNTs supported the existence of the dendrimer phthalocyanines on the SWNTs.

More evidence to support dendrimer phthalocyanines covalently on the SWNTs was found in the IR spectra. Fig. 3 showed the IR spectra of SWNTs, dendrimer phthalocyanines and dendrimer phthalocyanine chromophores-functionalized SWNTs nanoconjugates. A symmetrical C=O stretching at 1733 cm^{-1} was assigned to the vibration of COOH moieties on the SWNTs [25]. The vibration bands at 1640 and 1724 cm^{-1} match the amide groups of **SWNTs-E-16DZnPc** and **SWNTs-H-16DZnPc**. Furthermore, the IR spectra of **SWNTs-E-4ZnPc**, **SWNTs-H-4ZnPc**, **SWNTs-E-8DZnPc**, **SWNTs-H-8DZnPc** also showed other bands that are coincident with those displayed bands similar to those of **SWNTs-E-16DZnPc** and **SWNTs-H-16DZnPc** in Fig. S8.

Raman spectra provided essential and useful information that the dendrimer phthalocyanines have been successful covalently to the SWNT sidewalls. Fig. 4 showed the Raman spectra of the pristine SWNTs as well as the phthalocyanine functionalized nanoparticles **SWNTs-E-16DZnPc**, and **SWNTs-H-16DZnPc**. There