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Improved solubility and efficient optical limiting for methacrylate-co-porphyrins covalently functionalized single walled carbon nanotube nanohybrids

Aijian Wang[a,*], Laixiang Cheng[a], Wei Zhao[b], Weihua Zhu[a,**], Danhong Shang[c]

[a] School of Chemistry & Chemical Engineering, Jiangsu University, Zhenjiang, 212013, PR China
[b] School of Energy & Power Engineering, Jiangsu University, Zhenjiang, 212013, PR China
[c] School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212013, PR China

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ABSTRACT

To improve the dispersibility of single walled carbon nanotube (SWCNT) in common organic solvents and adjust its photoelectronic performance, two methacrylate-co-porphyrins covalently functionalized SWCNT nanohybrids (SWCNT-TPP **1** and SWCNT-TPP **2**) were prepared by radical polymerization. This attachment of porphyrins onto the surface of SWCNT significantly improves their solubility and dispersion stability of the SWCNT-based materials in organic solvents. The electronic interactions between porphyrins and SWCNT were investigated by the UV–vis, fluorescence and Raman spectroscopic methods. Z-scan measurements suggested that both nanohybrids exhibited increased nonlinear absorption and optical limiting performances compared to the separate SWCNT and porphyrins, which can be ascribed to the synergetic effects originating from the charge transfer effect between the two counterparts. The best optical limiting performance is observed for SWCNT-TPP **1** due to more effective charge transfer effect in comparison with those of other samples. These results suggest that the radical polymerization is a useful approach towards the rational design of solution-processible yet stable optical limiting materials, and this concept may be readily extended to other directional optoelectronic properties.

1. Introduction

Due to their extremely large aspect ratio and excellent electrical, mechanical, optical, and thermal properties, the single-walled carbon nanotubes (SWCNTs)-based materials have attracted significant interest [1,2]. However, the insolubility of the SWCNTs in most solvents and the difficulties of handling these highly intractable carbon nanostructures are restricting their real-life applications. Indeed, it still remains a significant challenge to realize nanometer-scale control over the percolating structures of SWCNTs with excellent photoelectric properties [3–5]. And thus substantial efforts have been dedicated to obtaining well-separated and functionalized SWCNTs, with the aim to overcome this difficulty and to efficiently manage their extraordinary properties [6–8]. In most cases, surface modifications of SWCNTs can be separated into two different approaches, i.e. covalent and noncovalent functionalizations [9,10]. Particularly, the covalent methods provide a high degree of versatility toward utilizing additional nanotube chemistry compared to the noncovalent ways, which can significantly influence their mechanical and electronic properties. The covalent attachment of appropriate moieties is anticipated to facilitate the development of applications by improving solubility and ease of dispersion, and also providing for chemical attachment to surfaces [11,12].

On the other hand, due to their large and fast optical limiting performance and capability to be readily engineered for a particular purpose, the photoelectronic functional materials with extensive π-electron delocalization have drawn considerable interest for the protection of human eyes, optical elements, or optical sensors from intense laser pulses [13]. Among these π-electron delocalization systems, porphyrins are an important family of conjugated organic compounds, which have a wide applicability in medicine, optics, electronics, and many other fields [14]. It has been reported that SWCNTs in suspension excited with laser pulses at 532 nm can behave as optical limiter, stemming from the strong nonlinear scattering effect [15,16]. In spite of the wide variety of materials that have been implemented for use as optical limiters, no single material or combination of materials has yet been identified as an ideal material capable of protecting any given optical

* Corresponding author.
** Corresponding author.
E-mail addresses: wajujs@ujs.edu.cn (A. Wang), sayman@ujs.edu.cn (W. Zhu).

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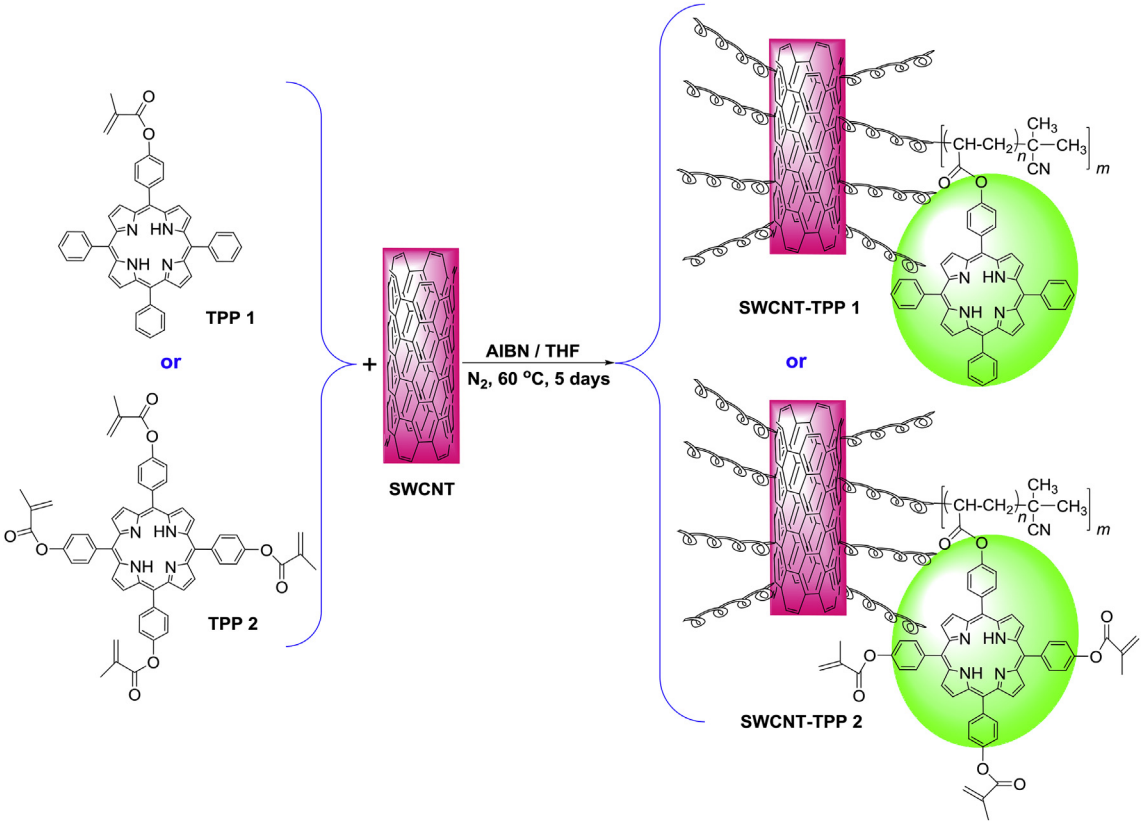

Scheme 1. Synthesis of porphyrin-covalently functionalized SWCNT nanohybrids (SWCNT-TPP **1** and SWCNT-TPP **2**).

equipment from a potential laser threat [17–19]. By covalent functionalizing SWCNTs with porphyrins as the product is generally expected to possess many of the intrinsic properties of porphyrins and SWCNTs, affording new and tunable optoelectronic properties. Increased nonlinear optical and optical limiting responses are thus to be expected from porphyrins functionalized SWCNTs nanohybrids, stemming from the additional scattering component and the interfacial interactions between two constituent parts.

We report here on the photophysical and nonlinear optical (including optical limiting) properties of SWCNT-porphyrins nanohybrids (Scheme 1). Using Raman and UV–vis spectra in combination with fluorescence emission spectroscopy, we explore the nature of the electronic interactions between SWCNT and porphyrins in more detail. The experimental demonstration of the electronic interactions between SWCNT and porphyrins provides a deeper understanding of the interfacial interactions, and alters the electronic structure and vibrational characteristics of the SWCNTs in the combined system. The nonlinear optical and optical limiting responses of SWCNT-porphyrins nanohybrids are found to incorporate the mechanisms of charge transfer between porphyrins and SWCNT, an aspect that has not been explored much in the literature.

2. Experimental section

2.1. Materials and reagents

All reagents were of chemical or analytical grade. The SWCNTs, with a length of 0.5–2 μm and a > 95% purity as well, were purchased from Beijing DK Nano technology Co., LTD (China). To ensure that SWCNTs are free of air and absorbed moisture prior to functionalization, they were dried under dynamic vacuum at 200 °C for 24 h and subsequently stored under N_2. The radical initiator 2,2′-azobisisobutyronitrile (AIBN) was obtained from Shanghai Sinopharm Chemical Reagent Co. Ltd, China, and used after recrystallization twice from methanol. Other chemicals were purchased from commercial suppliers and used as received unless otherwise stated. 5-[4-(Methacryloyloxy) phenyl]-10,15,20-triphenylporphyrin (TPP **1**) and 5,10,15,20-tetrakis (4-(methacryloyloxy)phenyl)porphyrin (TPP **2**) were obtained according to the literature procedures [20–22]. The details about instruments and nonlinear optical measurements are presented in Supporting information.

2.2. Synthesis of SWCNT-TPP 1

The radical polymerization reactions used to prepare the methacrylate-co-porphyrins covalently functionalized SWCNT nanohybrids were performed under N_2 atmosphere. A typical reaction is presented in Scheme 1. A mixture of SWCNT (40 mg), TPP **1** (80 mg) and THF (40 mL) was heated in a water bath at 40 °C and sonicated for 30 min; the mixture was purged with dry N_2 and then allowed to react at 66 °C under a blanket of N_2. The radical initiator AIBN (200 mg) was added in portions (5 × 40 mg every 24 h) over a period of 5 days. After this period, the resultant material was precipitated by addition of methanol and water, and then filtered through a 0.45 μm nylon membrane to isolate the carbon-based material, which was washed with deionized water, ethanol and then dichloromethane several times to remove excess TPP **1** and other contaminants. The product was dried overnight under vacuum at room temperature, affording the desired SWCNT-TPP **1** nanohybrid (50 mg).

2.3. Synthesis of SWCNT-TPP 2

SWCNT (40 mg) was added to a solution of TPP **2** (80 mg) and AIBN (200 mg) in THF (40 mL), and then was stirred at 66 °C under N_2 for 5 days. After this reaction, the handling procedures were as above for the SWCNT-TPP **1** nanohybrid.