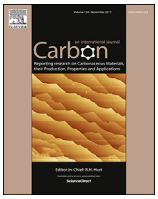
Carbon 124 (2017) 618–629

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon



Covalent-linked porphyrin/single-walled carbon nanotube nanohybrids: synthesis and influence of porphyrin substituents on nonlinear optical performance

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A R T I C L E I N F O

Article history:
Received 2 April 2017
Received in revised form
20 August 2017
Accepted 26 August 2017
Available online 28 August 2017

A B S T R A C T

Electron-withdrawing 4-cyanophenyl-, electronically innocent phenyl-, and electron-donating 4-dimethylaminophenyl-functionalized porphyrin/single-walled carbon nanotube (SWCNT) nanohybrids have been synthesized and characterized by ultraviolet–visible absorption, steady-state fluorescence, Fourier transform infrared, and Raman spectroscopies, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and thermogravimetric analysis. Nonlinear optical (NLO) studies using the Z-scan technique revealed that both the cyano (CN) and the dimethylamino (DMA) substituents have a positive effect in optimizing the optical limiting performance of the SWCNT–porphyrin nanohybrids, owing to increased reverse saturable absorption (RSA) of the porphyrin moieties after functionalization by CN or DMA. In comparison with CN, the DMA group has a more positive influence on the porphyrin excited states and thereby the RSA and NLO activity.

1. Introduction

Carbon nanoallotropes from 0D to 1D and 2D, examples of which include C60, single- and multiple-walled carbon nanotubes (CNTs), and graphene, respectively, have been intensively investigated within both the scientific and the industrial communities during the past two decades [1–3]. Special attention has been paid to single-walled CNTs (SWCNTs), which comprise a single graphene layer seamlessly wrapped into a cylindrical tube with an internal void [4–8]. The hexagonal lattice of sp^2 carbon atoms bestows excellent electrical, mechanical, thermal and optical properties on SWCNTs, making them favored candidates for applications in electronic/optical devices, catalysis, and nanomedicine, and as nanoreactors [9–13]. However, owing to high surface energy and significant π-π electron interactions between the tubes, SWCNTs have a high tendency to aggregate into bundles [4]. This gives rise to very limited solubility/dispersity of SWCNTs in organic solvents or water, creating a serious difficulty for processing and thus real-life applications. To solve this, surface functionalization of SWCNTs has been proposed, which might also introduce enhanced or novel properties, thereby leading to new applications for certain functional entities (e.g. inorganics, polymers, organic dyes, etc.) [14–18].

Porphyrin is a natural organic dye comprising a square-planar 18π-electron aromatic macrocycle. It possesses many appealing properties, such as high chemical and thermal stability, a large extinction coefficient in the visible light region, multiple stable cationic states, and strong reverse saturable absorption (RSA) for

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http://dx.doi.org/10.1016/j.carbon.2017.08.060

laser pulses in the visible region. These attributes equip porphyrins for use across a wide range of research fields [19–22]. In addition, the rich metal coordination chemistry as well as the readily available methods of chemical modification on the periphery of the porphyrin skeleton provides great flexibility for the synthesis of novel porphyrin-dyes with specific properties [23–25].

Recently, many reports have focused on combining SWCNTs with porphyrins to form inorganic/organic hybrid composites, and this has been shown to be a promising approach in the pursuit of photon-to-electron transfer, solar energy conversion, and nonlinear optical (NLO) applications [26–29]. In particular, the combination of porphyrins (exhibiting RSA) and SWCNTs (with strong nonlinear optical scattering (NLS) properties) results in interesting SWCNT-porphyrin (SWCNT–Pr) ns with enhanced optical limiting (OL) behavior, useful in the efficient extinction of potentially damaging high intensity light such as that from lasers [30]. The first nonlinear characterization of a SWCNT-porphyrin nanohybrid material [31], in which porphyrins spontaneously adhered to the nanotube surface in solution through non-covalent van der Waals interactions, revealed a strong nonlinear absorption effect with nanosecond pulses (Z-scan technique at 532 nm). Subsequent studies of π-π stacked SWCNT–Pr nanohybrids revealed an ultrafast OL response and a low limiting threshold from femtosecond nonlinear measurements at 780 nm [32]. In order to avoid possible dissociation and to ensure that the SWCNT–Pr nanohybrids are stable, several covalent linking methodologies have been examined [33–38]. Tian and coworkers reported that covalently-linked SWCNT–Pr has a lower linear absorption than the physically blended combination. Energy transfer (ET) and photo-induced electron transfer (PET) from porphyrins to SWCNTs play an important role in increasing the OL performance, with the π-conjugated bridge (phenylene) between the SWCNTs and the porphyrins resulting in much more efficient ET/PET than with amide or ester covalent linkages, and thereby a more efficient OL effect [30].

However, in sharp contrast to the great progress achieved in optimizing the NLO properties of purely organic porphyrins and metalloporphyrins through synthesis and modification [20,39,40], NLO research on covalently-linked SWCNT–Pr nanohybrids is sparse [34]; there is no report thus far on the influence of further chemical modification, especially at the organic porphyrin moiety, on the NLO performance of covalent SWCNT–Pr nanohybrids. In this work, we have designed and synthesized three novel SWCNTs covalently functionalized with *tert*-butyl substituted 5,10,15,20-tetraphenylporphyrins (TPPs), employing one classical organic electron-acceptor cyano group (CN) and one classical organic electron-donor dimethylamino group (DMA) attached at the opposite extremity of TPP to the SWCNTs (SWCNT–Pr2 and SWCNT–Pr3 respectively), as well as an example with an unmodified phenyl as control, SWCNT–Pr1 (Fig. 1). Thorough characterization was carried out by ultraviolet–visible (UV–vis) absorption, steady-state fluorescence, Fourier transform infrared (FTIR), and Raman spectroscopies, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA), which collectively unambiguously confirmed that the chosen porphyrins were successfully attached to the surface of the SWCNTs by a 1,2,3-triazole-containing π-conjugated covalent bridge rather than by non-covalent means. Nonlinear transmittance tests by the Z-scan technique (532 nm, 4 ns duration) revealed that both electron-withdrawing CN and electron-donating DMA substituents have positive effects in further optimizing the OL performance of the SWCNT–Pr nanohybrids, owing to the increased RSA ability of the porphyrin moieties after attaching CN or DMA. In comparison with CN, the DMA group has a more positive influence on the porphyrins' excited states and thus effectively further enhanced the RSA process and the final NLO performance of the SWCNT–Pr nanohybrids. This may provide a useful guide to the design of better NLO materials for device applications in optoelectronics and photonics.

2. Experimental

2.1. Materials and reagents

The pristine SWCNTs (*p*–SWCNTs) with average diameters of 1–2 nm and lengths of 0.5–2 μm were purchased from Beijing DK nano technology Co. Ltd. and used as received. All of the reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. All materials were of chemical or analytical grade. 5,15-bis-(3,5-bis{*tert*-butyl}phenyl)porphyrin 1 and 5-(4-aminophenyl)-10,20-bis-(3,5-bis{*tert*-butyl}phenyl) porphyrin 2 (Fig. 2) were prepared according to those reported literatures [41,42]. Tetrahydrofuran (THF) and diethyl ether were dried and distilled over sodium before use. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylamide (DMF), dimethylsulfoxide (DMSO), toluene, chloroform, dichloromethane (DCM), pyridine and triethylamine (TEA) were used without further purification.

2.2. Measurements

UV–visible absorption spectra (UV–vis) were recorded on TU-1901 spectrophotometer. Fluorescence spectra were obtained with a CARY Eclipse Fluorescence Spectrophotometer. FTIR spectra were recorded on a WQF-600N spectrometer. Raman spectra were measured using an inVia Raman microscope (Renishaw) with both the 532 and 785 nm lines of an Ar ion laser as excitation source. The X-ray photoelectron spectroscopy (XPS) experiments were performed on an ESCALAB250Xi system (ThermoFisher, USA) equipped with a monochromatic Al Kα (1486.6 eV) source and a concentric hemispherical energy analyser. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker (400 MHz) spectrometer using tetramethylsilane as internal standard. Mass spectral data were recorded on a Bruker Daltonics ultrafleXtreme MALDI-TOF/TOF. The water bath sonication was performed with a KQ-400KDE sonicator (400 W, 40 kHz, Kunshan Sonicator Instrument Co., Inc.). For thermogravimetric analysis (TGA), a TGA/1100SF instrument was used and samples were heated in an alumina pan in a dry nitrogen flow (20 sccm) to 600 °C at a rate of 10 °C $\min^{-1}$. Field emission scanning electron microscope and transmission electron microscope images were obtained on Hitachi/S-4800 and JEM-2100 instruments, respectively. All the measurements except TGA were carried out at room temperature.

The nonlinear optical properties of the samples were investigated using the open-aperture Z-scan technique with linearly polarized 4 ns pulsed 532 nm light generated from a mode-locked Nd:YAG laser with a repetition rate of 2 Hz; the absorption extinction coefficients were calculated by the theory reported previously [43]. The normalized transmittance $T_{\mathrm{Norm}}(z)$ as a function of position (z) is given by $T_{\mathrm{Norm}}(z) = \mathrm{Log}[1 + q_0(z)]/q_0(z)$, where $q_0(z) = \beta I_0 L_{\mathrm{eff}}/[1 + (z/z_0)^2]$, $L_{\mathrm{eff}} = [1 - \exp(-\alpha L)]/\alpha$, z_0 is the diffraction length of the beam, I_0 is the intensity of the light at focus, L_{eff} is the effective length of the sample, L is the true optical path length through the sample, and α is the linear absorption coefficient. The focal length was 400 mm. The DMF dispersions of the samples were placed in 5 mm thick quartz cells mounted on a computer-controlled translation stage, and then moved along the *z*-axis of the incident beam. The input energy and the transmitted energy were measured using two energy detectors (Rjp-765 Energy Probe), which were linked to an energy meter (Rj-7620 Energy Ratiometer, Laser Probe Inc.). A computer was used to collect and