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Enhanced Optical Limiting Effects in Porphyrin-Covalently Functionalized Single-Walled Carbon Nanotubes**

By Zhi-Bo Liu, Jian-Guo Tian,* Zhen Guo, Dong-Mei Ren, Feng Du, Jian-Yu Zheng,* and Yong-Sheng Chen

Optical limiters are employed to protect sensitive optical components or eyes from laser-induced damage.^[1,2] They have lower transmittance for high-intensity or fluence laser input while they keep a high linear transmittance. Many works have concentrated on creating ideal optical limiting devices by exploiting passive limiting mechanisms such as nonlinear absorption (multiphoton absorption, reverse saturable absorption (RSA)), nonlinear refraction (electronics or thermal effects), and nonlinear light scattering. Both single-walled carbon nanotube (SWNT) and multiwalled carbon nanotube (MWNT) suspensions have been reported to have strong optical limiting effects in the nanosecond regime, which arise from strong nonlinear light scatterings due to the creation of new scattering centers consisting of ionized carbon microplasmas and solvent microbubbles.^[3–9] To promote their optical limiting effects, the optical nonlinear media with other optical nonlinear processes (e.g., two-photon absorption or RSA) have been blended with carbon nanotubes.^[10,11] The association of SWNTs with organic chromophores having multiphoton absorption processes was recently shown to be a promising approach to achieve optical limiting systems with broad temporal and spectral responses.^[10] Carroll et al.^[11] also reported an enhanced nonlinear transmittance obtained by a RSA dye blended with carbon nanotubes. Recently, Blau et al.^[12] presented a study on nonlinear optical characterization of stable porphyrin/SWNT composite solutions obtained by non-covalent

bonding between the carbon nanotubes and conjugated tetraphenylporphyrin molecules.

However, little research has been carried out on optical limiting effects of covalently functionalized SWNTs with reverse saturable absorbers. Vivien et al.^[5] predicted that further optimizations of the optical limiting performances of carbon nanotubes may be achieved by the cumulative influences of different nonlinear effects arising from functionalized carbon nanotubes with reverse saturable absorbers. Porphyrins are often used as visible chromophores to decorate the surfaces of semiconductor and metal nanoparticles, and they are also promising candidates for applications in optical limiters owing to their large RSA in the visible even near-infrared wavelength range.^[13–15] Furthermore, an effective energy or electron transfer may exist in the functionalized SWNTs with porphyrins.^[16] The photoinduced electron transfer can result in a large optical limiting effect, which has been observed in the PVK-modified SWNTs system.^[17,18] We also reported that a covalently 5-*p*-aminophenyl-10,15,20-triphenylporphyrin-functionalized SWNTs exhibits a strong optical limiting.^[19] In this Communication, we present the large enhancement of optical limiting effects in three covalently functionalized SWNTs with porphyrins at 532 nm, and the contribution of photoinduced electron or energy transfer to enhanced optical limiting is discussed.

The structures of porphyrin-functionalized SWNTs, SWNT-TPP (**I**), SWNT-NH-TPP (**II**), and SWNT-SnDPP (**III**) are shown in Figure 1. The SWNT sample was produced by using the arc-discharge method with NiO/Y₂O₃ as catalyst.^[20] According to the established relationship between radial breathing mode (RBM) frequency and tube diameter,^[21] individual tubes have a diameter range of 1.4–1.7 nm. 5,10,15,20-tetraphenylporphyrin (TPP), 5-*p*-aminophenyl-10,15,20-triphenylporphyrin (NH₂TPP) and trans-dihydroxo [5,15-bis-(3,5-diethoxyphenoxy)porphyrin]Tin(IV) (Sn(OH)₂DPP) were also prepared for a comparison of their optical properties with functionalized SWNTs'. Further details of the SWNTs' functionalization can be found in the Experimental section.

Shown in Figure 2 are the absorption and fluorescence spectra of TPP, NH₂TPP, Sn(OH)₂DPP, **I**, **II**, and **III** in *N,N*-dimethylformamide (DMF) solutions. It is seen from the absorption spectrum of **I** shown in Figure 2a that its Soret band and Q-band have 5 nm and 4–7 nm red-shift relative to TPP in DMF respectively, and its Soret band has a notable broadening relative to the porphyrin moiety. A similar notable

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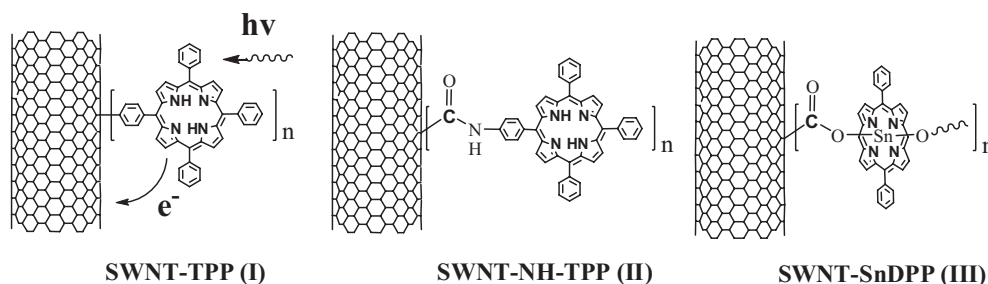


Figure 1. Structures of porphyrin-covalently functionalized SWNTs I, II, and III.

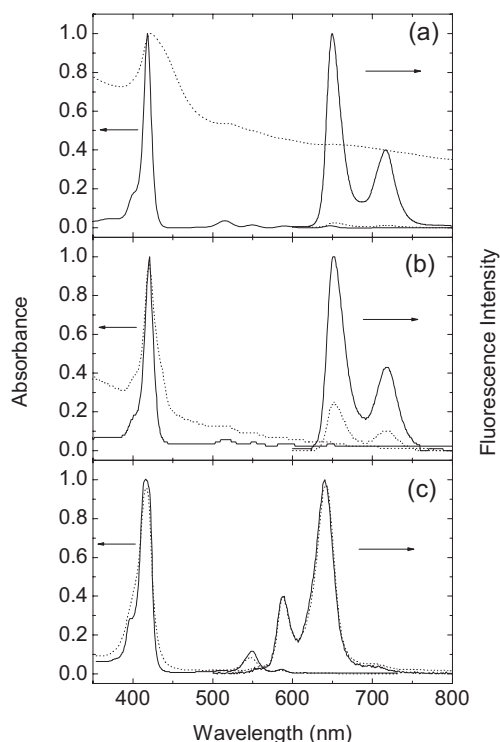


Figure 2. Absorption and fluorescence spectra of a) **I** (dotted line) and TPP (solid line), b) **II** (dotted line) and NH₂TPP (solid line), c) **III** (dotted line) and Sn(OH)₂DPP (solid line).

broadening of the Soret band in **II** relative to the porphyrin moiety can be observed as shown in Figure 2b, however, there is no red-shift of the Soret band. The UV-vis absorption spectrum of **III** (Fig. 2c) is similar to that of Sn(OH)₂DPP because the effect of carbon nanotube absorption on the porphyrin peak positions is relatively small.^[16] In order to probe excited state interactions of porphyrins and SWNTs, the fluorescence spectra of **I**, **II**, **III**, TPP, NH₂TPP and Sn(OH)₂DPP were measured, as shown in Figure 2a. Upon excitation of the porphyrin moiety in Soret band, the solution of **I** exhibits 97 % quenching of fluorescence emission at 651 nm and 717 nm. The fluorescence spectrum of **II** has the same profile as that of TPP, but its fluorescence quantum yield is only about 25 % of that of NH₂TPP (Fig. 2b). Therefore, the magnitude of

fluorescence quenching of **I** is larger than that of **II**. The previously reported porphyrin–nanotube hybrids linked by flexible chains^[16] exhibits the excited-state energy transfer quenching of porphyrin fluorescence caused by SWNTs, which is dependent on the length of the tether linking the porphyrin moiety to the nanotube. However, as the linkage chains become shorter no fluorescence quenching occurs.^[16] **III** has a shorter tether linking the porphyrin ring to SWNTs than **II**, thus both its fluorescence spectral profile and intensity hardly changed from Sn(OH)₂DPP to **III**, indicating that almost no fluorescence quenching occurred (Fig. 2c). For the composite **I**, the effective quenching can be explained by the extended conjugated π -system of SWNTs with a porphyrin-mediated through-bond mechanism owing to the unique direct linkage mode of the two moieties.^[22,23] A possible pathway to the deactivation of excited porphyrin can be attributed to two competitive processes, energy transfer (ET) and photo-induced electron transfer (PET).

Since it was predicted that the further optimizations of optical limiting performances of nanotubes may be achieved by the accumulation of different nonlinear effects by functionalizing carbon nanotubes with reverse saturable absorbers,^[5] we performed the nonlinear transmittance measurements to compare optical limiting effects of porphyrin-functionalized SWNTs. The characteristics of output fluence vs. input fluence for these samples are shown in Figure 3a, and the curves of nonlinear transmittance vs. input fluence are shown in Figure 3b. C₆₀ solution in toluene was employed as a reference. For comparison, all of the samples were set to have same linear transmittance of 75 % at 532 nm by adjusting their concentration. From Figure 3, it can be seen that the optical limiting effects of three porphyrins functionalized SWNTs (**I**, **II**, and **III**) are much better than not only C₆₀ and SWNTs, but also these individual porphyrins (TPP and Sn(OH)₂DPP). The optical limiting thresholds of **I**, **II**, and **III** are approximately 70, 100, and 150 mJ·cm⁻², respectively, all of which are much smaller than those of C₆₀ (300 mJ·cm⁻²) and SWNTs (250 mJ·cm⁻²). At the highest fluence (95 mJ·cm⁻²) used in our experiments, the transmittance has decreased to 4.3 %, 5.1 %, and 6.6 % for **I**, **II**, and **III**, respectively, while the transmittance is 11.3 %, 9.9 %, 21 %, and 33.5 % for C₆₀, SWNTs, TPP, and Sn(OH)₂DPP, respectively. This illustrates that enhanced optical limiting effects can be

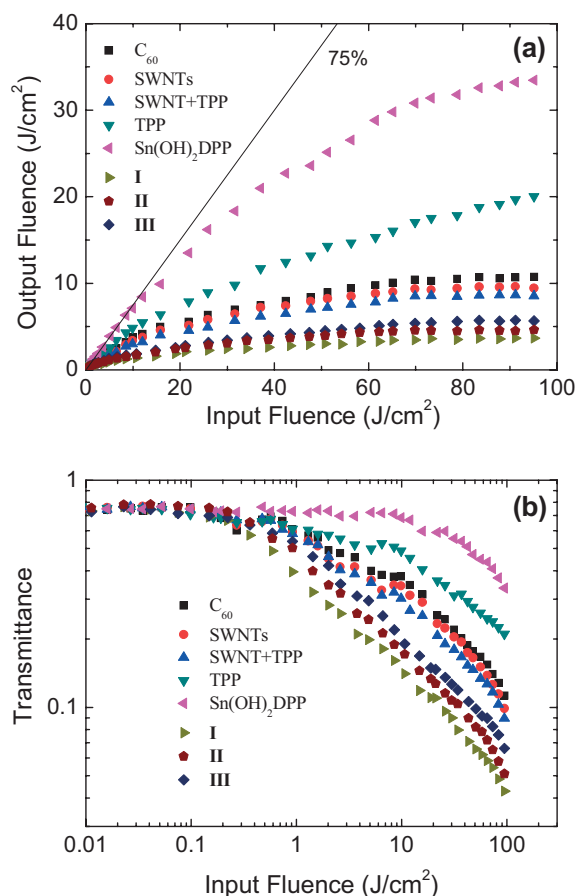


Figure 3. The optical limiting of C₆₀, SWNTs, SWNT+TPP, TPP, Sn(OH)₂DPP, I, II, and III for 5-ns pulsed laser at 532 nm. a) Output fluence vs. input fluence. b) Nonlinear transmittance spectra vs. input fluence. The linear transmittance for all of the samples was adjusted to 75 %.

obtained by functionalizing SWNTs with RSA chromophore porphyrins.

As we know, nonlinear transmittance can be enhanced by blending a RSA dye with carbon nanotubes.^[11] To compare functionalized SWNTs with blended system, we also performed the optical limiting measurements of SWNTs blended with TPP, as shown in Figure 3. Because the content of porphyrin in **I** was about 30 %, which was determined by thermogravimetric analysis^[24] and the fittings of the absorption spectra of SWNTs and **I**, the sample of 7:3 weight ratio of SWNTs to TPP was used as the blended system, and its linear transmittance was also adjusted to 75 % at 532 nm. The optical limiting effect of SWNT+TPP blended system is better than those of C₆₀, SWNTs, and TPP, since the shortcomings of these individual materials' optical limiting are compensated by combining these materials into a single system.^[11] However, the functionalized SWNTs with porphyrin may be more suitable for the application in optical limiting than SWNT+TPP blended system as shown in Figure 3. In SWNT+TPP blended system, although nonlinear transmittance can be available enhanced by complementary nonlinear

mechanisms, linear absorption has been also increased simultaneously. Under same concentrations of 20 mg·L⁻¹, the linear transmittances of **I** and SWNT+TPP are 70 % and 55 %, respectively. The increase of linear absorption can partially restrict the enhancement of optical limiting effect.

To get a better insight into the optimizations of the optical limiting performances of porphyrin functionalized SWNTs, we carried out open-aperture Z-scan experiments of SWNTs, SWNT+TPP, **I**, **II**, and **III** with the same concentration of 20 mg·L⁻¹, and results are shown in Figure 4a. The linear transmittances of SWNTs, SWNT+TPP, **I**, **II**, and **III** are 64 %, 55 %, 70 %, 68 %, and 75 %, respectively. The composite **I** has a largest dip among the transmittance curves of these materials, indicating that it should have the best optical limiting effect. Although the combination of nonlinear scattering with RSA can improve the optical limiting effect effectively, we believe that the enhanced limiting performance arises from not only the combination of nonlinear mechanism, but also the photoinduced electron or energy transfer from electron donor TPP moiety to acceptor SWNTs.^[17,18] From Figures 2 and 3, it can be seen that **I** with stronger fluorescence quenching (about 97 %) has a better optical limiting effect than **II** (about 75 %). This photoinduced electron transfer could produce a charge-separated excited state and result in a

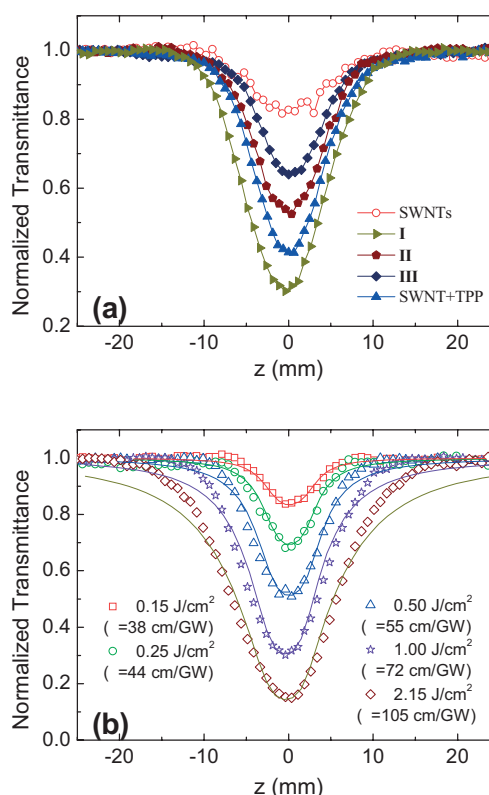


Figure 4. Open-aperture Z-scan curves for 5ns pulsed laser at 532 nm. a) Z-scan curves of SWNTs, SWNT+TPP, **I**, **II**, and **III** with same concentration of 20 mg·L⁻¹. b) Z-scan curves of **I** for different input fluence. The solid lines are the numerical fittings.

large optical limiting effect, just as the semiconducting polymer/methano-fullerene system reported previously.^[25] Comparatively there is almost no fluorescence quenching occurring in the composite **III**, and the enhancement of optical limiting effect for **III** is the smallest among three functionalized SWNTs.

Figure 4b gives the open-aperture Z-scan curves of **I** for different input fluence. Using the Crank–Nicolson finite-difference scheme, we fitted the Z-scan curves numerically (the solid lines) and obtained the values of nonlinear absorption coefficient, β , as shown in Figure 4b. In general, the value of β will decrease as input fluence increases for RSA process because of the saturation of RSA,^[26] and however it will keep unchanged for two-photon absorption process. The increase of β with input fluence implies that besides nonlinear absorption the observed optical limiting performance is also influenced by nonlinear scattering in the high-fluence regime. The similar phenomena were also observed in the composites **II** and **III**. In SWNTs and porphyrin non-covalent blended system, the nonlinear absorption coefficient β will decrease as intensity increases.^[12] This may be due to the saturation of the accessible energy levels under high-intensity pumping.

In summary, functionalizing SWNTs with RSA chromophores porphyrins can enhance optical limiting performance. The porphyrins covalently functionalized SWNTs offer superior performance to C₆₀, the individual SWNTs and porphyrins by combination of nonlinear mechanism and the photoinduced electron or energy transfer between porphyrin moiety and SWNTs. Further studies to understand better the mechanism and the structure–property correlations are currently in progress.

Experimental

SWNT-TPP: The SWNTs sample was produced by arc-discharge method. It was purified via oxidative acid treatment according to an established procedure. 6.3 mg of purified SWNTs was sonicated for 4 h in 7.5 mL *o*-dichlorobenzene (ODCB). To this suspension was added 20 mg (0.032 mmol) 5-*p*-aminophenyl-10,15,20-triphenylporphyrin (NH₂TPP) in 2.0 mL of acetonitrile. After transfer to a septum-capped flask and bubbling with nitrogen for 10 min, 10 μ L (0.074 mmol) of isoamyl nitrite was quickly added and the suspension was stirred in dark at 70 °C under the protection of nitrogen for 48 h. Another 100 mg (0.16 mmol) 5-*p*-aminophenyl-10,15,20-triphenylporphyrin and 50 μ L (0.37 mmol) isoamyl nitrite were added in 5 times (total 5 \times 20 mg TPP-NH₂ and 5 \times 10 μ L isoamyl nitrite) during this period to ensure high degree of functionalization. After cooling to room temperature, the suspension was diluted with 10 mL *N,N'*-dimethylformamide (DMF), filtered over a nylon membrane (0.1 μ m), and washed extensively with DMF. Sonication and redispersion were repeated in DMF and then in ether to remove the adsorbed porphyrin and solvent. The final product was collected by filtration over a nylon membrane (0.1 μ m) and dried in vacuum at 80 °C for 10 h to give modified SWNTs as black powder (5.8 mg).

SWNT-NH-TPP: The SWNTs were treated as the same above. After the oxidation process, about 10 % (Weight) of carboxylic acid groups were introduced to the surface and end of SWNTs. Then purified SWNTs sample was treated with thionyl chloride at 70 °C for 24 h. After the complete removal of excess thionyl chloride, porphyrin [5-(4-aminophenyl)-10,15,20-triphenylporphyrin] was added, the

DMF solution was stirred in the presence of triethylamine at 100 °C under nitrogen protection for 2 days. The functionalized SWNTs were isolated by washing off the unreacted porphyrin with a large amount of chloroform on 0.2 μ m pore size nylon membrane, with the help of sonication to disperse the solid, the removal of free porphyrin was accomplished via washing with diluted acetic and triethylamine, finally with chloroform. The product was then dried at 60 °C for 9 h under vacuum.

SWNT-SnDPP: The SWNTs were treated as the same above. In a typical Sn(OH)₂DPP porphyrin covalent solubilization experiment, a purified SWNT sample (49 mg) was added to a solution of Sn(OH)₂DPP in THF (10 mg mL⁻¹, 10 mL), and the mixture was sonicated for 48 h. After the removal of THF on a rotary evaporator, the solid mixture was extracted repeatedly with hexanes, coupled with vigorous centrifuging, to remove free Sn(OH)₂DPP. Then, THF was added to the solid sample to dissolve the SnDPP-attached SWNTs. Upon vigorous centrifuging, the solid residue was collected and then used to go through the same covalent solubilization procedure again. The soluble SWNT–SnDPP samples from the two repeated experiments were combined, followed by a complete evaporation of the solvent THF, the residue was dried at 60 °C for 9 h under vacuum.

Measurements: The optical limiting and Z-scan experiments were preformed with linearly polarized 5 ns pulses at 532 nm generated from a frequency doubled Q-switched Nd:YAG laser. The spatial profiles of the pulses were of nearly Gaussian distribution after the spatial filter. The pulses were split into two parts. The reflected pulse was used as reference, and we focused the transmitted pulse onto the sample by using a 150 mm focal length lens. The sample was placed at the focus where the spot radius of the pulses was (25 \pm 2) μ m. The reflected and transmitted pulse energies were measured simultaneously with two energy detectors (Moletron J3S-10). C₆₀ was employed as a standard. For optical limiting experiments, all of the sample concentrations were adjusted to have same linear transmittance of 75 % at 532 nm in 5 mm quartz cells. For Z-scan experiments, the samples have same concentration of 20 mg·L⁻¹.

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