Allyloxyporphyrin-Functionalized Multi-Walled Carbon Nanotubes: Radical Polymerization Synthesis and Enhanced Optical Limiting Properties

Aijian Wang,^[a] Yu Fang,^[b] Wang Yu,^[a] Lingliang Long,^[a] Yinglin Song,^[b] Wei Zhao,^[a] Marie P. Cifuentes,^[c] Mark G. Humphrey,^[c] and Chi Zhang^{*,[a]}

Abstract: Allyloxyporphyrin-functionalized multi-walled carbon nanotubes (MWCNT-TPP) were synthesized by the radical polymerization and characterized by Fourier-transform infrared spectroscopy, ultraviolet/visible absorption, and X-ray photoelectron spectroscopies, elemental analysis, transmission electron microscopy and thermogravimetric analysis. Z-scan studies reveal that this

nanohybrid exhibits enhanced nonlinear optical (NLO) properties compared to a control sample comprising a non-covalently-attached physical blend of MWCNTs and porphyrin, as well as to the individual MWCNTs and porphyrin.

Keywords: porphyrin • multi-walled carbon nanotubes • radical polymerization • nonlinear optical properties

At the wavelengths used, the mechanism of enhanced optical limiting likely involves reverse saturable absorption, nonlinear scattering and photo-induced electron/energy transfer effect between the MWCNTs and the porphyrin. The role of electron/energy transfer in the NLO performance of MWCNT-TPP has been investigated by Raman and fluorescence spectroscopies.

Introduction

If laser beams are to be deployed more widely in daily life, highly effective optical limiting (OL) materials that protect human eyes and various delicate optical devices from strong laser threats are needed urgently.^[1-3] An ideal optical limiter should have a lower transmittance for high-intensity laser input while exhibiting high transmittance for low-intensity optical input.^[4] The lack of nonlinear optical (NLO) materials has been a significant barrier to the development of such devices. To this end, considerable research efforts have been invested in OL materials and processes (including organic and inorganic materials), in an attempt to achieve some measure of protection from such laser beams.^[5-10] A plethora of applications have been suggested for OL materials, so it is critically important to explore and evaluate innovative NLO materials required for the practical applications.^[8]

From the perspective of carbon nanostructures as OL materials,

fullerenes,^[1,11]

graphene,^[12]

graphitic nanoplates,^[13]

single-walled carbon nanotubes^[14]

(SWCNTs

) and multi-walled carbon nanotubes (MWCNTs),^[15-16] as well as their derivatives, have attracted significant interest from chemists and material scientists because of their electronic, mechanical, optical and chemical characteristics. Among these materials, MWCNTs have been seen as one of the best candidates for electron donor-acceptor (D-A) ensembles, due to their large number of concentric graphitic tubes.^[17-18] A convenient route to prepare a D-A ensemble is to link a soluble polymer or oligomer as donor and MWCNTs as acceptor via a covalent bond. This method is anticipated to facilitate applications' development by improving solubility and ease of dispersion, and to improve their OL performances through a synergistic effect.^[19-20] The covalent functionalization of MWCNTs is most frequently initiated by introducing carboxylic acid groups using a nitric acid oxidation approach; these acid groups are then converted into other functional groups.^[21] However, this covalent attachment may damage the perfect structure and mechanical properties of MWCNTs, thereby potentially affecting the properties of the resultant MWCNT-based nanohybrid materials.^[22] Thus, developing a facile as well as efficient chemical modification approach is unambiguously desirable for preparing high-performance MWCNT-reinforced nanohybrids.

Suspensions of MWCNTs have been reported to have strong OL effects in the nanosecond regime. These effects result from the strong nonlinear light scattering by the new scattering centers that derive from the thermally induced formation of ionized carbon microplasmas and solvent microbubbles,^[23] similar to those in carbon black suspensions.^[24] Unlike MWCNTs, porphyrins and their numerous analogues generally exhibit strong nonlinear absorption properties because they possess higher excited-state

[a] Dr. A. J. Wang, W. Yu, Dr. L. L. Long, W. Zhao, Prof. Dr. C. Zhang
China-Australia Joint Research Center for Functional Molecular Material
Scientific Research Academy
Jiangsu University, Zhenjiang 212013 (P.R. China)
Fax: (+86)-511-88797815
E-mail: chizhang@ujs.edu.cn

[b] Prof. Dr. Y. L. Song, Y. Fang
School of Physical Science and Technology
Soochow University, Suzhou 215006 (P.R. China)

[c] Prof. Dr. M. G. Humphrey, Dr. M. P. Cifuentes
Research School of Chemistry
Australian National University
Canberra, ACT 0200 (Australia)

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Scheme 1. Synthesis of the MWCNT-TPP and MWCNT-AIBN nanohybrids.

absorption cross-sections than ground-state absorption cross-sections; they also have high architectural flexibility, which makes them ideal materials that can fulfill many of the requirements of potential OL applications.^[25-28] Indeed, association of the nonlinear scattering properties of carbon nanostructures with the reverse saturable absorption (RSA) properties of organic chromophores has been shown to be a promising way to prepare ideal NLO materials.^[29-31]

Encouraged by these considerations, we expected that the combination of MWCNTs and optoelectronic porphyrins would afford species that possess not only the intrinsic properties of MWCNTs and porphyrins, but also some functions resulting from the mutual π interaction between the MWCNTs and the porphyrins; multifunctional nanohybrid systems with increased OL performance compared with that of the individual MWCNTs and porphyrin may thereby be generated. In this contribution, we report that the direct reaction of an asymmetrically-substituted metal-free allyloxyporphyrin with MWCNTs by radical polymerization in the presence of azobisisobutyronitrile (AIBN) affords covalently functionalized MWCNT-TPP nanohybrids. These nanohybrids were fully characterized by various spectroscopies, and enhanced NLO properties and OL effects of the resultant species were observed, compared to those of a control sample comprising a non-covalently-attached physical blend of MWCNTs and porphyrin, and the individual MWCNTs and porphyrin.

Results and Discussion

Syntheses: The covalent reaction of MWCNTs with polymers is important due to the fact that long polymer chains may help to improve the solubility of the nanotubes in a wide range of solvents, even at a low degree of functionalization, while maintaining nanotube isolation.^[32] This can be achieved through either the “grafting from” or “grafting to” methodologies.^[33-34] In the former,

covalent immobilization of the polymer precursors on the surface of MWCNTs and subsequent polymerization occurs in the presence of monomeric species. During the radical polymerization process, double bonds on the surface of the MWCNTs are opened by initiator molecules and the MWCNTs surface plays the role of the grafting agent. The “grafting to” method is based on the synthesis and end-group transformation of a polymer followed by its attachment to the MWCNTs. However, the preparation of end-functionalized polymers, which is necessary for the “grafting to” method, has some difficulties.^[35] The “grafting from” approach has the advantage of minimizing interference with the elaborate molecular framework, and thereby reduces the likelihood of compromising the nanotube’s physical attributes. In the present study, MWCNTs were successfully modified with polystyrene chains by a radical polymerization reaction, confirming that MWCNTs can be activated by free radical initiator molecules to open their π -bonds for polymerization.^[32] To the best of our knowledge, this is the first report introducing conjugated polymers with porphyrin units on the surface of MWCNTs through radical polymerization. Scheme 1 summarizes the procedures for the preparation of the MWCNT-TPP and MWCNT-AIBN nanohybrids. In this reaction, the MWCNTs were modified in bulk quantities with allyloxy-functionalized porphyrin through thermolysis of the AIBN to form radical reactive intermediates that can then react with the surface of the MWCNTs to form covalent bonds. The monomer allyloxy-functionalized porphyrin was synthesized by an adaptation of a pre-existing literature procedure.^[36] The nanohybrids were then prepared by radical polymerization of the MWCNTs with AIBN in THF, either in the presence or absence of the allyloxy-functionalized porphyrin (Scheme 1), and washed with water, methanol and cold acetone several times to remove excess porphyrin and other contaminants; the as-prepared nanohybrids can be dispersed in polar solvents such as DMF and DMSO to form black suspensions.

Figure 1. FTIR spectra of TPP, MWCNT-TPP, MWCNT-AIBN and as-received MWCNTs.

Fourier Transform Infrared Spectroscopy: Fourier transform infrared (FTIR) spectra can convincingly confirm the functionalization of MWCNTs.^[37] Figure 1 displays the FTIR spectra of TPP, MWCNT-TPP, MWCNT-AIBN and as-received MWCNTs, after subtraction of the KBr contribution. As shown in the spectrum of the MWCNTs, the presence of multiple bands across the range 2880-2900 cm^{-1} is consistent with the presence of $-\text{CH}_n$ species (i.e. $-\text{CH}$, $-\text{CH}_2$ and $-\text{CH}_3$).^[38, 39] The peak at 1683 cm^{-1} is attributed to the MWCNT's skeletal motions. The bands at 1400-1600 cm^{-1} and near 1200 cm^{-1} are assigned to $\text{C}=\text{C}$ stretching and $\text{C}-\text{O}$ stretching modes, respectively, which originate from the inherent structure of carbon nanotubes. Following functionalization with porphyrins and AIBN, the relative intensity of the $-\text{CH}_n$ species increases significantly, consistent with the presence of additional $-\text{CH}_n$ species. Simultaneously, some bands consistent with the presence of porphyrin were also observed in the range 480-1500 cm^{-1} , which proves the successful functionalization of the MWCNTs. It should be noted that the interaction between MWCNTs and porphyrin or AIBN is not a simple physical adsorption, because both resultant hybrids were washed vigorously multiple times.

Figure 2. Raman spectra of MWCNT-TPP, MWCNT-AIBN, and as-received MWCNTs.

Raman Spectroscopy: The surface functionalization of the MWCNTs was further confirmed by Raman spectroscopy (Figure 2).

The D-band at 1344 cm^{-1} and G-band at 1574 cm^{-1} for the as-received MWCNTs correspond to the disordered graphitic structure or sp^3 -hybridized carbons of the nanotubes, and to a removal of the degeneracy of the E_{2g} stretching mode of graphite, respectively.^[40] Because of the presence of amorphous carbon and impurities in the as-received MWCNTs, the D-band is more intense than the G-band, with an intensity ratio (I_D/I_G) of 1.14. The D- and G-bands of MWCNT-TPP, which appear at 1350 and 1579 cm^{-1} , respectively, are red-shifted compared to those of pristine MWCNTs, due to electron transfer from TPP to MWCNTs. No obvious shift was observed for MWCNT-AIBN. The relative intensities of bands in the spectra of MWCNT-TPP and MWCNT-AIBN are much greater than those in the spectrum of MWCNTs. The relative intensity ratios (I_D/I_G) for MWCNT-TPP and MWCNT-AIBN are 0.75 and 0.91, respectively, both significantly smaller than that of the as-received MWCNTs (1.14). Recent work by Wang et al.^[41] on the functionalization of MWCNTs with poly(xylylviologen) found that the intensity ratio (I_D/I_G) decreased from 1.97 to 1.76 following functionalization, consistent with our results. These changes can possibly be assigned to the organic molecules grafted to the surface of the MWCNTs, resulting in an increase in absorption intensity of the sp^2 -hybridized carbon atoms,^[42] any increase in the D band intensity due to functionalization possibly being more than offset by a simultaneous decrease because of purification.^[43] In addition to the D- and G-bands, it should be noted that similar results are observed for the second-order mode of the D band (2677 cm^{-1} for the MWCNTs, 2684 cm^{-1} for MWCNT-TPP, and 2682 cm^{-1} for MWCNT-AIBN). Further studies are needed to understand completely the effects of covalent functionalization of MWCNTs on the intensity of Raman signals.

Linear Absorption Spectroscopy: The presence of TPP (or AIBN) in the MWCNT-TPP (or MWCNT-AIBN) nanohybrid materials was further confirmed by linear optical absorption spectroscopy. The absorption spectra of TPP, MWCNT-TPP, MWCNTs and MWCNT-AIBN in DMF solutions are shown in Figure 3. The electronic absorption spectrum of TPP is characterized by an intense Soret band at 418 nm, and relatively weaker Q bands between 490 and 638 nm, consistent with spectra of porphyrin analogues.^[44-45] MWCNTs exhibit a broad absorption maximum at 270 nm with continuously intensity extending to 638 nm. After functionalization,

it can be seen from the absorption spectrum of MWCNT-TPP shown in Figure 2 that its Soret band and Q band have been red-shifted 3 and 5 nm, respectively, compared to that of TPP in DMF. Its Soret band is suppressed and has a notable broadening relative to the porphyrin moiety, as a consequence of the possible electronic interactions between the MWCNTs and porphyrin moieties in the system (TPP is usually regarded as an electron donor and MWCNTs as electron acceptors).^[31] It has been reported that the electronic interactions between CNTs and chromophores result in red-shifts of the optical absorption maxima for the chromophores upon attachment to the CNTs' surfaces.^[46] The peak maxima of MWCNTs in MWCNT-AIBN and MWCNT-TPP nanohybrids are red-shifted by $\Delta\lambda = 4$ and 2 nm, respectively. Despite the aforementioned spectral features, the spectral window between the Soret and Q bands is still clearly evident, indicating that the MWCNT-TPP nanohybrid is suitable for OL of 532 nm laser light. These observations are consistent with the formation of nanohybrids and with the tunability of optical properties through different substitution, as well as notable electronic communication between the π -systems of MWCNTs and porphyrin in the ground state.

Figure 3. UV/Vis absorption spectra of TPP, MWCNT-TPP, MWCNT-AIBN and MWCNTs in DMF.

Fluorescence Spectroscopy: With the aim of probing the excited-state electronic interactions of porphyrin moieties and MWCNTs, the fluorescence spectra of MWCNT-TPP, TPP and MWCNT/TPP blends were measured, the results being shown in Figure 4. Upon excitation of the porphyrin moiety in the Soret band (418 nm), MWCNT-TPP exhibits emission peaks at 652 and 719 nm that originate from the S_1-S_0 transition. Because MWCNTs do not exhibit a fluorescence signal, the fluorescence of MWCNT-TPP must be from the TPP moieties. The emission intensity at 652 nm of TPP in the MWCNT-TPP nanohybrid is decreased by 30% in comparison to that of the free TPP, indicating that MWCNT-TPP undergoes fluorescence quenching, a result likely to arise from a through-bond mechanism because of the unique direct linkage of the porphyrin moieties and the MWCNTs. In contrast, when compared to pure TPP, the emission intensity of TPP in this nanohybrid at 719 nm is increased by 126%. Following excitation at the same wavelength, the control sample (MWCNTs/TPP blends) shows similar emission bands with a 10% quenching of fluorescence emission in comparison with that of TPP. These suggest that the quenching of porphyrin in MWCNT-TPP is more effective than the control samples, and provide further evidence for the covalent grafting. Experimental results and molecular orbital theory have demonstrated that due to their unique π -electron systems, CNTs are

favorable electron acceptors when directly connected to an appropriate electron donor.^[18] In the present MWCNT-TPP nanohybrid, it is reasonable to believe that following photoexcitation the intramolecular donor-acceptor electronic interactions between the two moieties of TPP and MWCNTs may involve an electron and/or charge transfer from the excited singlet TPP to the MWCNT, resulting in the observed fluorescence quenching and energy release (Figure 4). These nanohybrids therefore have potential as the active material for various optoelectronic applications, such as sources for solar energy harvesting in solar cells.

Figure 4. Fluorescence spectra of MWCNT-TPP, TPP and blended MWCNTs and TPP in DMF, following excitation at 418 nm.

Figure 5. TGA curves of MWCNTs, TPP, MWCNT-AIBN and MWCNT-TPP. Experiments were performed in highly purified N_2 . Heating rate: $10^\circ C\ min^{-1}$.

Thermogravimetric Analysis: Thermogravimetric analysis (TGA) has been widely used to characterize the covalent chemical functionalization of MWCNTs.^[47] The thermodynamic properties of TPP, MWCNTs, MWCNT-AIBN and MWCNT-TPP were investigated by TGA under a N_2 atmosphere (Figure 5). TPP shows poor thermal stability, with an onset decomposition temperature of $75^\circ C$, and exhibits a total loss of about 63%. The TGA curve of the MWCNTs displays a loss of weight of about 7.23% between 150 and $700^\circ C$, which is ascribed to the destruction of the residual amorphous carbon still present in the nanotubes and to the decarboxylation of the oxidized species, but may also arise from the organic and inorganic impurities trapped in the MWCNTs.^[48] Because of the coating of AIBN, the functionalized MWCNTs (MWCNT-AIBN) exhibit a significant weight loss from 200 to $800^\circ C$ (about 34% at $800^\circ C$). The MWCNT-TPP hybrid is

thermally less stable than the individual MWCNTs and TPP. When heated to 800 °C, about 68% weight loss was observed for MWCNT-TPP, which may result from the dissociation of covalently bound TPP moieties. As can be seen in Figure 5, the weight loss curves of the TPP and MWCNT-TPP samples are very similar, consistent with successful grafting of TPP to the MWCNTs.

Table 1. Elemental compositions of MWCNTs, MWCNT-TPP and MWCNT-AIBN calculated from combustion analysis.

Content (w/%)	C	N	H
MWCNTs	96.56	—	0.20
MWCNT-TPP	78.76	8.45	7.64
MWCNT-AIBN	88.58	4.14	2.46

Elemental Analyses and X-ray Photoelectron Spectroscopy: In order to confirm the elemental composition and ascertain further electronic information, X-ray photoelectron spectroscopy (XPS) spectra of pristine MWCNTs, MWCNT-AIBN and MWCNT-TPP were obtained. In each case, the gross elemental composition of the sample on the quartz substrate surface was established via an initial broad scan from 200 to 800 eV (Figure 6). All samples exhibit C1s and O1s peaks, but increased O content and the appearance of a N1s peak are observed in the spectra of MWCNT-AIBN and MWCNT-TPP, indicating that some organic molecules have been successfully grafted onto the MWCNT surface.^[49] This can be further confirmed by the high-resolution C1s spectra of MWCNTs, MWCNT-AIBN and MWCNT-TPP (Figure S2). It can be clearly seen that the intensity of the C1s peaks of MWCNT-AIBN and MWCNT-TPP dramatically decrease, compared with that of as-received MWCNTs. These suggest the great effect of chemical treatments on the MWCNTs surface. Elemental combustion data for MWCNTs, MWCNT-TPP and MWCNT-AIBN are shown in Table 1. The oxygen element content can be obtained by assuming that the remaining content is oxygen only. MWCNTs contain a majority of C (96.56%) with a very low content of H (0.20%) and O (3.24%), the latter ascribed to the ambient atmospheric moisture tightly bound to the MWCNTs.^[50] The atomic percentages of H 7.64 % (or 2.46%) and N 8.45% (or 4.14%) for MWCNT-TPP (or MWCNT-AIBN) are significant compared to those of MWCNTs and consistent with the FTIR and TGA results, suggesting that the MWCNTs are functionalized by TPP (or AIBN).

Figure 6. XPS spectra of MWCNTs, MWCNT-AIBN and MWCNT-TPP.

Transmission Electron Microscopy: Transmission electron microscopy (TEM), which can reveal morphological differences, is a powerful tool for characterizing nanohybrids.^[51] The microstructures of pristine MWCNTs and the chemically modified MWCNTs (MWCNT-TPP and MWCNT-AIBN) are shown in Figure 7. The morphology of the pristine MWCNTs is quite typical, with a chaotic orientation of distinguishable single nanotubes that have relatively smooth and clean surfaces (Figure 7a and 7b). In contrast, the MWCNT-TPP hybrid, shown in parts c and d of Figure 7, appears stained with TPP, which results in the wall of the modified MWCNTs appearing thicker, similar to the appearance of the previously-reported functionalized MWCNTs with isocyanate and isophthaloyl chloride groups.^[52] The morphology of TPP bound to the surface of the MWCNTs is a function of the allyloxyporphyrin degree of polymerization, the coverage of the MWCNT with allyloxyporphyrin polymer being non-uniform (Figure 7c). Similar results were observed for MWCNT-AIBN. However, the average outer diameter of the MWCNT-TPP nanohybrids is larger than the MWCNT-AIBN examples, as shown in parts d and f of Figure 7, which correlates with the lower organic content found by TGA in the latter sample, as well as with the results of elemental analyses. Figure 7g and 7h display the high-resolution transmission electron microscopy (HRTEM) images of raw MWCNTs and MWCNT-TPP composites. For pristine MWCNTs, the external surface of MWCNTs is well crystallised and corresponds to graphene layers. On the contrary, it is obvious that surfaces of MWCNT-TPP are covered by an amorphous layer exhibiting a thickness between 3 and 5 nm (Figure 7h). These layers correspond to the grafted polymer chains, suggesting the efficient grafting of allyloxyporphyrin, as observed by the presence of diffuse hazy contrast at the walls. Therefore, the MWCNT-TPP composite has the typical core (MWCNTs)-shell (allyloxyporphyrin polymer) structures. In addition, the structure of MWCNT-TPP composite was clearly observed using HRTEM because of the different densification of MWCNTs and allyloxyporphyrin polymer layers.

Nonlinear Optical Studies: The Z-scan method, which measures the optical nonlinearities through detecting the far-field sample transmittance of a focused Gaussian beam as a function of sample position (z), is a well-known and convenient experimental technique to characterize the NLO properties of materials.^[53-54] In the present case, OL performance measurements for all samples were carried out using the open-aperture Z-scan technique at 532 nm with 4 ns laser pulses (Figure 8). MWCNTs have been taken as the reference for comparing the OL effects of the various dyes, as reported previously.^[55] For ease of comparison, all samples were adjusted to have the same linear transmittance (53% at 532 nm) by varying their concentration.

The OL responses of MWCNT-AIBN, TPP, and MWCNT-TPP in DMF solution are compared to those of a suspension of MWCNTs in Figure 8, in which the output fluence was plotted as a function of input fluence. Because the OL curves are obtained by direct conversion from the Z-scan data, there are no additional errors included in the OL results.^[56] As shown in Figure 8, all samples display a similar trend, that is, the output fluence increases linearly with the input fluence by obeying Beer's law at low incident energies, and deviates from linearity as the input fluence increases indicating the occurrence of an OL effect.^[57-58] The decrease in output fluence of MWCNT-TPP with increasing fluence exceeds that of all other samples in the present study. The extent of the decrease in output fluence (MWCNT-TPP > TPP > MWCNT-AIBN > MWCNTs) suggests that the OL performance of MWCNT-TPP is

Figure 7. (a) and (b) TEM images of pristine MWCNTs; (c) and (d) TEM images of MWCNT-TPP; (e) and (f) TEM images of MWCNT-AIBN; HRTEM images of (g) MWCNTs and (h) MWCNT-TPP.

better than those of the MWCNT-AIBN and the individual porphyrin and MWCNTs. Under the measurement conditions, pure DMF displays no detectable OL performance, so the solvent contribution is negligible, and the observed OL properties can be attributed to the solutes alone.

It is well-known that the OL properties can be increased by blending carbon nanotubes with RSA organic chromophores,^[59] so to compare the MWCNT-TPP nanohybrid with such blended system, the OL measurements of MWCNTs blended with allyloxyporphyrin (TPP) were also performed (Figure 8). As expected, the output fluence of the MWCNT/TPP blended system is lower than MWCNTs and TPP, which is consistent with its better OL performance, but inferior to the new porphyrin-functionalized MWCNTs. The covalent attachment of allyloxyporphyrin moieties is anticipated to facilitate applications' development by improving solubility and ease of dispersion, and also providing for chemical attachment (polymer matrices) to surfaces, in an attempt to allow for the fabrication of device required for the use of nanotubes in a real OL application. Good interfacial adhesion between the MWCNTs and the allyloxyporphyrin polymer (Figure 7) is essential for efficient load transfer in the composite.^[21] But the forces between the wrapping molecules and the MWCNTs in the blended system are very weak, suggesting that the load may not be transferred efficiently from the polymer to the MWCNTs. In addition, the insoluble nature of MWCNTs makes it difficult to study their molecular properties and limits their fabrication for practical applications. Therefore, the MWCNTs nanohybrid covalently functionalized by allyloxyporphyrin is better candidates for applications in OL than the blended system, and the individual porphyrin and MWCNTs.

As discussed above, all samples are optical limiters, so to gain further insight into optimization of the OL responses of porphyrin-functionalized MWCNTs, the nonlinear absorption behavior of MWCNTs, MWCNT-AIBN, TPP, blended MWCNTs and TPP, and MWCNT-TPP in DMF was evaluated by the Z-scan method under an open-aperture configuration using 4 ns and 21 ps pulsed laser irradiation at 532 nm with an intensity of 0.4 μJ . The valley-shaped curves indicate the occurrence of nonlinear absorption, and an OL behavior.^[60-63] The depth of the valley in the Z-scan curves correlates with the extent of OL. It is clear that OL is significantly enhanced following porphyrin attachment to the MWCNTs (Figure

9), so the MWCNT nanohybrid covalently functionalized by porphyrin is a better candidate for OL applications than the individual porphyrin or MWCNTs. Moreover, the indication of optical saturation was observed in the topmost curve of Figure 9. In this case, the samples display saturable absorption (SA) effect at a relatively lower input fluence, while switching to RSA as the sample approaches to the focal point. The switching from SA to RSA may be due to a consequence of competition between ground state bleaching (SA) and nonlinear absorption.^[64-65] When the input laser is moderate, majority of the MWCNTs nanoparticles are pumped into excited state and left behind many empty states, resulting in a smaller population of the plasmon band (the ground state bleaching of the plasmon band).^[66-67] When the laser intensity further increases, the nonlinear absorption starts to play a dominant role since it is more sensitive to the excitation intensity, and therefore RSA was observed at high excitation intensity.^[68] Remarkably, by increasing the input fluence to 2.0 from 0.4 μJ , as shown in Figure S3, a valley within the peak appears at the focal point and becomes deeper increasingly, which indicates that RSA appears and finally a nonlinear absorption occurs in MWCNTs, similar to the appearance of the previously-reported NLO properties of graphene oxide^[69], gold nanocubes^[70] and silver nanodots^[71].

Figure 8. Optical limiting responses (to 4 ns, 532 nm optical pulses) of MWCNTs, MWCNT-AIBN, TPP, blended MWCNTs and TPP, and MWCNT-TPP in DMF.

Figure 9. Open-aperture Z-scan curves of MWCNTs, MWCNT-AIBN, TPP, blended MWCNTs and TPP, and MWCNT-TPP at 532 nm with (a) 4 ns and (b) 21 ps pulse duration.

Three mechanisms are likely contributors to the increased NLO properties of the MWCNT nanohybrid: RSA from the chromophore, nonlinear scattering from the MWCNTs, and photo-induced electron/energy transfer from the chromophore to the MWCNTs.^[72] The porphyrin chromophore is a good candidate for an OL device due to the strong RSA that originates from excited-state absorption (ESA). In the ESA process, the porphyrin has a larger excited-state than ground-state absorption. As the input fluence increases, more porphyrin molecules are promoted to the excited state, resulting in higher absorption at intense excitation.^[73] The OL mechanism of MWCNTs is dominated by nonlinear scattering, the same mechanism as that exhibited by carbon black suspension.^[74] In this scattering process, heating from the laser pulses leads to vaporization and ionization of the MWCNTs, and the resultant rapid formation of micrometer-sized plasmas.^[75-76] These microplasmas strongly scatter light from the transmitted beam direction, leading to the limiting effect. Indeed, during our measurements, the MWCNT-TPP nanohybrid exhibited enhanced nonlinear scattering when traversing towards the focal point of the laser pulse. Several systems studied earlier (e.g. phthalocyanine-functionalized graphene and porphyrin-functionalized SWCNT suspensions) have been reported to possess enhanced OL responses, attributed to a combination of mechanisms including strong nonlinear scattering.^[14,77] This unusually efficient OL behavior is not an intrinsic feature of the individual MWCNT domains, but is related to the interaction with their environment. Detailed Raman and fluorescence spectra of porphyrin-functionalized MWCNTs have provided clear evidence for electron/energy transfer from porphyrin to MWCNTs, facilitating nonlinear transitions in the considerably larger density of states in the MWCNTs, and thereby contributing to the overall OL effect;^[78] this suggestion is verified in the present case by the Z-scan of the blended system.

Conclusions

A porphyrin-functionalized MWCNT nanohybrid material (MWCNT-TPP) has been prepared through radical polymerization reactions and its NLO responses have been studied using the Z-scan method at 532 nm. Significant fluorescence quenching of the porphyrin dyes following covalent bonding to the MWCNTs is observed, due to energy transfer from the excited porphyrins to the MWCNTs. MWCNT-TPP dispersions display better OL performance than their individual precursors, a blended system of MWCNT and TPP, and the control sample; this is proposed to result from a combination of RSA, nonlinear scattering and a photo-induced electron/energy transfer effect. The photo-induced electron/energy transfer effect has been confirmed by Raman and fluorescence spectra. These results suggest that porphyrin-functionalized MWCNT nanohybrids can have potential applications in eye and sensor protection and in photonics. Further investigations, with the aim of developing solid materials for ultrafast all-optical processing, are currently underway.

Experimental Section

Materials and reagents

MWCNTs with an average diameter of 20-30 nm and length of 10-30 μm were purchased from the Beijing DK Nanotechnology Co. Ltd, China, and used as received with a purity of 95%. The radical initiator AIBN was obtained from Shanghai Sinopharm Chemical Reagent Co. Ltd, China, and used after recrystallization twice from methanol. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Other reagents were purchased from commercial suppliers and used without further purification. All reactions were performed under nitrogen (N_2) atmosphere with the use of standard Schlenk techniques. Allyloxyporphyrin 5-(4-allyloxy)phenyl-10,15,20-triphenylporphyrin (TPP) was prepared by a method similar to the procedures reported in the literature.^[36]

Instruments and measurements

Fourier transform infrared (FTIR) spectra were recorded with a MB154S-FTIR spectrometer (Canada) using spectroscopic grade KBr pellet. Raman spectra were recorded at room temperature on a Renishaw InVia Raman Microscope, excited at 532 nm with Ar^+ radiation. The laser light was focused onto samples by using a microscope equipped with an $\times 100$ objective. The ultraviolet/visible (UV/Vis) spectral measurements were obtained with a JASCO V-570 spectrophotometer. Steady-state fluorescence spectra were acquired with a Fluoro-Max-P instrument. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 system from 50 to 700 $^{\circ}\text{C}$ under a N_2 atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Samples of ca. 1.3 mg were measured in an alumina crucible. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a RBD upgraded PHI-5000C ESCA (Perkin-Elmer) with Mg K α radiation ($h\nu = 224.0 \text{ eV}$). Elemental analyses were obtained on a Perkin-Elmer 240C CHN elemental analyzer. TEM and HRTEM experiments were performed with a JEM-2100 (JEOL) working at 200 kV. Samples for TEM analysis were obtained by spreading a drop of a dilute dispersion of the as-prepared products on amorphous carbon-coated copper grids, which were then dried in air before being transferred into the TEM sample chamber. Column chromatography was performed with silica gel (100-200 mesh, Qingdao Haiyang Chemical Co. Ltd, China).

The nonlinear absorption properties of all samples (including MWCNT-TPP, MWCNT-AIBN, a MWCNTs/TPP mixture (3:2 weight ratio), TPP, and MWCNTs) were assessed by the Z-scan measurement with linearly polarized 4 ns and 21 ps pulsed light generated from a mode-locked Nd:YAG 532 nm laser with a repetition rate of 2 Hz. DMF solutions of all samples in quartz cells of 2 mm thickness were placed at the focal point of a lens with a focal length of 40 or 30 cm which was controlled by a computer, and then moved along the z-axis of the incident beam. The incident and transmitted laser pulses were measured by two energy detectors (Rjp-765 energy probe), which were linked to an energy meter (Rj-7620 ENERGY RATIONETER, Laserprobe).

Investigation of the OL performances of all samples was performed by the Z-scan technique with the same laser system as in the nonlinear absorption experiments. The intensity of the incident energy was varied continuously by using a polarizer-analyzer

combination. The whole output energy was captured by a large aperture photodetector maintained at a 10 cm distance from the OL materials. Curves of output fluence vs input fluence were obtained in this experiment. To avoid the influence of cumulative thermal effects, the laser pulses were fired at a low frequency of 2 Hz, to ensure that each pulse of light encountered fresh sample.

Synthesis of MWCNT-TPP and MWCNT-AIBN nanohybrids

The radical polymerization reactions employed to prepare the porphyrin- and AIBN-functionalized MWCNT hybrids were carried out under N₂ atmosphere. A typical reaction is shown in Scheme 1. To a 50 mL three-necked glass reactor was added MWCNTs (50 mg) and 10 mL THF. The mixture was placed into a water bath at 40 °C and sonicated for 10 min; AIBN (40 mg) and TPP (50 mg) were then added to the resultant mixture. The mixture was purged with dry N₂ and then allowed to react at 66 °C for 4 days under a blanket of N₂. After the reaction was complete, the flask was allowed to cool to room temperature while stirring was maintained. The resultant material was precipitated by addition of methanol and water, and then filtered through a 0.45 µm nylon membrane. The solid was collected and washed with water, methanol and cold acetone several times to remove excess TPP and other contaminants. The products (MWCNT-TPP) were dried under vacuum at room temperature for 36 h. Polymerization of MWCNTs and AIBN in the absence of TPP was also carried out for comparison. After the reaction, the handling procedures were as above for the MWCNT-TPP nanohybrid, affording the MWCNT-AIBN nanohybrid.

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The Table of Contents

Radical polymerization for MWCNT-TPP nanohybrid with enhanced nonlinear properties

Aijian Wang, Yu Fang, Wang Yu, Lingliang Long, Yinglin Song, Wei Zhao, Marie P. Cifuentes, Mark G. Humphrey, and Chi Zhang*

Allyloxyporphyrin-Functionalized Multi-Walled Carbon Nanotubes: Radical Polymerization Synthesis and Enhanced Optical Limiting Properties

Allyloxyporphyrin-functionalized multi-walled carbon nanotubes (MWCNT-TPP) were synthesized by the radical polymerization. The enhanced optical nonlinearities were observed for such a MWCNT-TPP

nanohybrid compared to a control sample comprising a non-covalently-attached physical blend of MWCNTs and porphyrin, as well as to the individual MWCNTs and porphyrin.

Supporting Information

Allyloxyporphyrin-Functionalized Multi-Walled Carbon Nanotubes: Radical Polymerization Synthesis and Enhanced Optical Limiting Properties

Aijian Wang,^[a] Yu Fang,^[b] Wang Yu,^[a] Lingliang Long,^[a] Yinglin Song,^[b] Wei
Zhao,^[a] Marie P. Cifuentes,^[c] Mark G. Humphrey,^[c] Chi Zhang*^[a]

[a] Dr. A. J. Wang, W. Yu, Dr. L. L. Long, W. Zhao, Prof. Dr. C. Zhang
China-Australia Joint Research Center for Functional Molecular Materials
Scientific Research Academy
Jiangsu University, Zhenjiang 212013 (P.R. China)
Fax: (+86)-511-88797815
E-mail: chizhang@ujs.edu.cn

[b] Prof. Dr. Y. L. Song, Y. Fang
School of Physical Science and Technology
Soochow University, Suzhou 215006 (P.R. China)

[c] Prof. Dr. M. G. Humphrey, Dr. M. P. Cifuentes
Research School of Chemistry
Australian National University
Canberra, ACT 0200 (Australia)

Figure S1. Fluorescence spectrum of MWCNTs in DMF, following excitation at 418 nm.

Figure S2. High resolution C1s XPS spectra of as-received MWCNTs, MWCNT-AIBN and MWCNT-TPP.

Figure S3. Open-aperture Z-scan curve of MWCNTs at 532 nm with 4 ns pulse duration at an intensity of 2 μJ .