J Mater Sci (2008) 43:5692–5701
DOI 10.1007/s10853-008-2826-4

REVIEW

Recent research progress on optical limiting property of materials based on phthalocyanine, its derivatives, and carbon nanotubes

Lei Zhang · Li Wang

Received: 25 April 2008 / Accepted: 24 June 2008 / Published online: 28 July 2008

Abstract Carbon nanotubes and organic compounds with extensive delocalized π-electron system such as phthalocyanine and its derivatives are attracted much attention as potential optical limiting materials. In this article, the optical limiting properties of carbon nanotubes, phthalocyanine as well as its derivatives and modifying approaches to improve their optical limiting performance are reviewed. In addition, the optical limiting properties exhibited by the nanohybrids obtained from the combination between carbon nanotubes and phthalocyanine or its derivatives are also introduced.

Introduction

The interaction between materials and high-intense electromagnetic field brought about from high-power laser pulse changes the input optical parameters such as frequency and swing, which is referred as nonlinear optical effect [1]. Nonlinear optical (NLO) materials based on above optical response have an important application in the manipulation of optical signals in optical communication and other optical signal processes. Optical limiting (OL) phenomenon, a kind of nonlinear optical effect, is attracting much attention in the protection of eyes and photoelectric devices against laser with the development in the laser technology. Since the first discovery of optical limiting phenomenon, much work has been done in the exploration of designing and synthesizing materials with excellent optical limiting property. Over the last decade, many researches had focused on materials with weak ground-state absorption and strong excited-state absorption based on reverse saturable absorption (RSA) [2, 3].

NLO material acting as an optical limiter strongly attenuates intense optical beams and performs low transmittance under high-intensity illumination while the optical passes through the limiter material linearly at lower light intensities. Ideally, the output energy passing through the limiter rises linearly with input until reaching the limiting threshold, which is defined as the point at which the transmittance is 50% of the initial transmittance (Fig. 1). Over the threshold, the output energy is localized at a determinate value in a certain intensity range. When the input influence intensity excess the saturated energy density, the optical limiting device will be destroyed and input optical transmit linearly. So far, the mechanisms of nonlinear optical limiting mainly include about nonlinear absorption, nonlinear refraction, and nonlinear scatting. [4].

Optical limiting responses resulting from nonlinear absorption are brought about by reverse saturable absorption or two photon absorption. Reverse saturable absorption is usually involved in metal clusters, metal phthalocyanine [5], fullerene, and their derivatives. The absorption section of these materials in excited states is bigger than that in the ground state [6, 7]. As a result, when the optical intensity is high, the media absorption coefficient increases with the input fluence intensity. Nonlinear optical property observed in some materials such as semiconductor can be explained with two photon absorption [5]. In this process, the particle absorbs two photons simultaneously at the higher light intensity and transits from the ground state to high-energy excitation states [4]. The materials involved in two photon

L. Zhang · L. Wang (✉)
State Key Laboratory of Chemical Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China
e-mail: opl_wl@dial.zju.edu.cn; hodgeyu@163.com

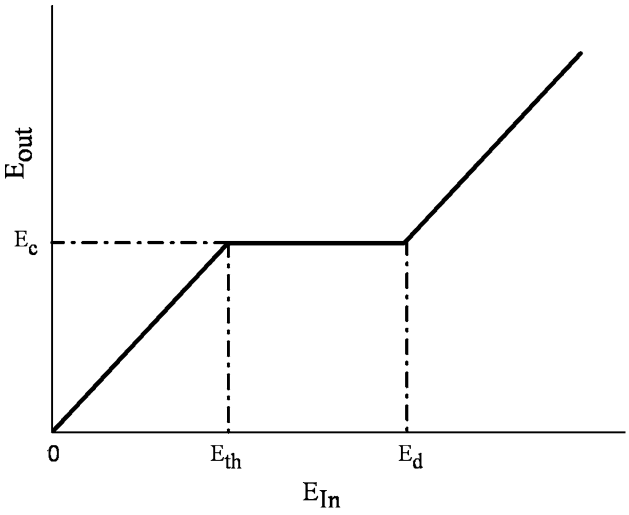


Fig. 1 The curve of ideal optical limiting [4]

absorption usually possess small absorption coefficient and high limiting threshold.

In addition, there are also other mechanisms such as nonlinear refraction and nonlinear scattering. The nonlinear refraction based on the optical effect of self-focusing and self-defocusing arises from the variety of refractive index when the media is exposed to laser. The nonlinear scattering attributed to the formation of ionized carbon microplasmas and solvent microbubbles acting as the scattering center due to heating of absorbing particles in the solution is usually recognized as dominant effect for the optical limiting mechanism of carbon black and carbon nanotubes suspension.

Generally, the potential optical limiting materials such as nanotubes, phthalocyanine, porphyrin, and their derivatives possess inherently special structure, for example, extensive delocalized π-electron system. Phthalocyanine (Pc) and its derivatives are usually centrosymmetric planar organic molecules with a two-dimensional conjugated π-electron ring. Due to their extensive π-electron delocalization, these molecules can display a strong nonlinear optical response [8]. On the other hand, their unique abilities of flexible modifying axially or peripherally also make them excellent candidates for optical device applications [9–11]. The surface of carbon nanotubes consists of hexahydric cycle structure in which a single pair of electron assigned to carbon atom delocalize in the system. So, nanotubes, phthalocyanine, porphyrin, and their derivatives with special conformation attract more and more attention as potential optical limiting materials.

There are some papers or reviews about the optical limiting property of phthalocyanine, porphyrin, and their derivatives [12–14]. Much work is mentioned in the papers to improve the optical limiting effect through the addition of metal into the center cavity of phthalocyanines or their derivatives and peripheral or axial substitution of some groups. Besides, the optical limiting properties of single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) are also discussed in some articles [5, 15–17]. It has been shown that the suspension of SWNTs or MWNTs exposed to the irradiation under high intensity at 532 and 1064 nm exhibits optical limiting effect which is usually attributed to nonlinear scattering due to the formation of carbon microplasmas and solvent microbubbles acting as the scattering centers [18–21]. The work about modification on the nanotubes to meliorate their limiting property has been continuously carried out [22–26] Recently, some groups pay attention to the combination of phthalocyanine, their derivatives, and carbon nanotubes due to their unique nonlinear optical responses and some better optical limiting effect are observed in the materials [6, 27–29].

This review is based on the recent research progresses about optical limiting properties exhibited by phthalocyanine, their derivatives, and carbon nanotubes and introduces their optical limiting property simply. The essential parts in this review introduce various modifications on the phthalocyanine, their derivatives, and carbon nanotubes to improve their optical limiting effect.

The nonlinear optical limiting properties of phthalocyanines and their derivatives

Generally, optical limiting responses exhibited by organic molecules are usually related to highly delocalized π-electron systems. Excellent optical limiting responses are reported in many articles on the phthalocyanines and their derivatives. Phthalocyanines and their derivatives with extensive two-dimensional π-electron system fulfill this requirement and have been attracted much attention as a promising NLO material. A variety of substituent groups can be used to modify the phthalocyanines peripherally and axially. It is found that the variety of metal inserted into the center cavity and peripheral or axial substitution have effect on their optical limiting property. These compounds hold other additional advantages, for instance, exceptional stability and favorable processable features. In virtue of the Z-scan technique with picosecond pulses at 532 nm, it is established that the nonlinear absorption in this type of compound mainly arises from excited singlet state absorption [30]. Much research work has been devoted to the development of new phthalocyanines with outstanding optical limiting capabilities by modification with different routes. For example, it has been demonstrated that the insertion of heavy atoms into the phthalocyanine ring causes significant effects on reverse saturation absorption (RSA) and optical limiting performance for nanosecond laser pulses, since they increase the intersystem crossing rate from singlet state to trivalent state [31].

The optical limiting property of phthalocyanines with different metal in the central cavity

Blau had experimentally measured some series of structurally different phthalocyanine derivatives containing Zn(II), Co(II), Ni(II), Pd(II), Pb(II), Ga(III), and In(III) [9]. It was found that the type of metal inserted into the center cavity of phthalocyanines had effect on the nonlinear optical property. One group of the phthalocyanines discussed are those compounds with same substitution, $–C_6H_{13}$, peripherally and different metal atom, Pd, Pb, and Ni. The structures of those compounds are shown in Fig. 2.

It is found that the phthalocyanine **1**, $(C_6H_{13})_8PcPd$, exhibits outstanding NOL and the largest value of nonlinear absorption coefficient, β_I, compared with phthalocyanine **2**, $(C_6H_{13})_8PcPb$, phthalocyanine **3**, $(C_6H_{13})_8PcNi$ and phthalocyanine **4**, $(C_6H_{13})_8PcPH_2$ [9]. These phthalocyanine compounds with the same peripheral substituents at the same site exhibit different ability of nonlinear absorption. The $(C_6H_{13})_8PcPd$ has a much lower saturation energy density, F_{sta}, than other compounds. Interestingly, the ratio of the absorption cross section, κ, is also small for palladium compound, the value of κ for the $(C_6H_{13})_8PcNi$ is smallest and $(C_6H_{13})_8PcPb$ is largest among these compounds with the same peripheral substituents [9].The κ coefficient for the phthalocyanine **1**, $(C_6H_{13})_8PcPd$, is nearly 2.7 times smaller than that for lead compound, and approximately 2.5 times larger than that for the nickel compound [9]. It is not easy to estimate which Pc will be the better optical limiter judged merely by the value of κ. In other words, the ratio of the absorption cross section does not characterize the strength of the nonlinear absorption distinctly.

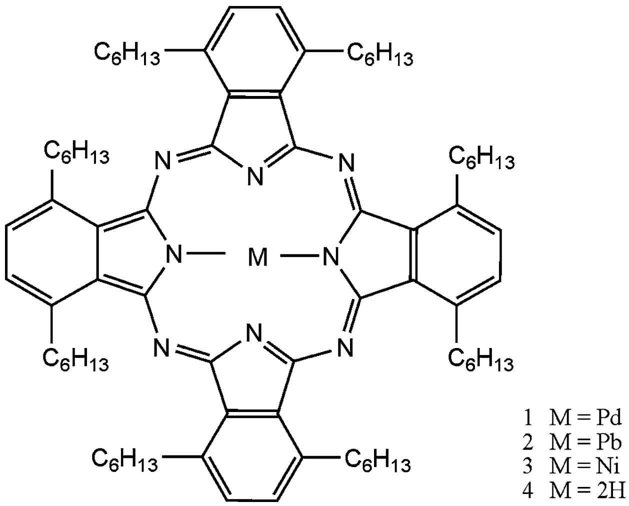


Fig. 2 The structure of the phthalocyanines with same substitution but different central atom M = Pd(II) Pb (II) Ni (II) 2H [9]

Introducing nickel into the central cavity does not bring about desirable effects in term of optical limiting, even the unsubstituted phthalocyanine **4**, $(C_6H_{13})_8PcPH_2$ has a much stronger nonlinear optical response than the nickel compound. It is obvious that $(C_6H_{13})_8PcPd$ exhibits the best nonlinear response in curve of transmission versus pulse-energy density while the nickel compound, $(C_6H_{13})_8PcNi$, possesses the weakest optical limiting response [9]. Substituting metal Pb into phthalocyanine has little positive effect on the nonlinear response and will not improve obviously the ability of optical limiting.

Among all the phthalocyanine compounds measured in Blau's work, the $(tBu)_4PcInCl$ compounds have the largest ratio of the absorption cross section, κ. But its saturation energy density, F_{sta}, is also large (24.2 ± 0.8 J cm^{-2}) [9].

The optical limiting property of phthalocyanines with different substitution axially

Recently, there are some reports discussing about substituting phthalocyanine axially at the central metal to improve optical limiting [12, 13]. The results obtained from them show that axial ligand can bring about considerable enhancement in optical limiting. The effect associated with the increased permanent dipole moment perpendicular to the macrocylce in the axially substituted phthalocyanine is possibly responsible for this phenomenon [14].

Aggregation is generally adverse in an optical limiting material since strong intermolecular interactions usually alter the excited state relaxation time and the effective nonlinear absorption of the material [12]. Suppression on unfavorable aggregation is important to improve the optical limiting capability. Compared with the chloro ligand $(tBu)_4PcMCl$, the aryl substituents $(tBu)_4PcM$ (*p*-TMP) can mitigate the packing behavior of the molecules in the solid state and aggregation in solution (Fig. 3). The aryl-substituted phthalocyanines, $(tBu)_4PcIn$ (*p*-TMP), with larger nonlinear absorption coefficient α at $\lambda > 550$ nm, exhibit a much lower threshold for optical limiting and a much lower transmission at high fluence than the compound with chloro substituents, $(tBu)_4PcInCl$ [12, 14].

In the gallium phthalocyanine case, $(tBu)_4PcGa$ (*p*-TMP), the value of saturation energy density, F_{sta}, is smaller than that of the $(tBu)_4PcGaCl$ while both have almost the same value of the ratio of the absorption cross section, κ, and the difference in the effect resulting from the substitution on nonlinear absorption coefficient β_I is also inconspicuous [14]. The value of F_{sta} for $(tBu)_4$ PcGaCl is nearly equal to 27.0 ± 1.0 J cm^{-2} [9]. The F_{sta}

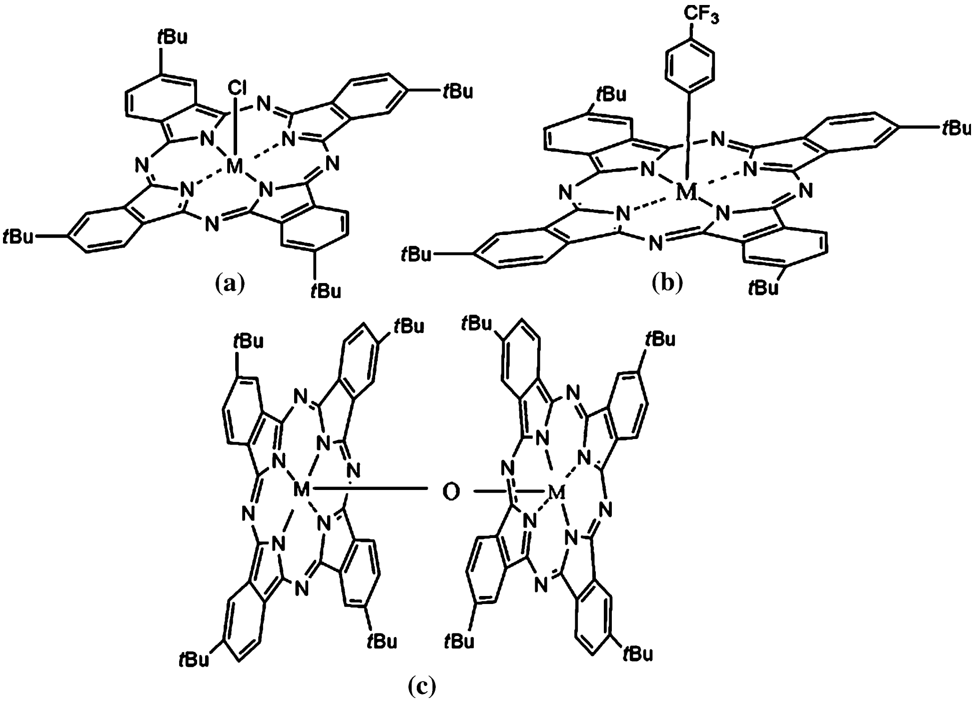


Fig. 3 (**a**) Phthalocyanines with chloro ligand, (tBu)$_4$PcMCl [M = Ga(III) (**1**), In(III) (**2**)], (**b**) phthalocyanines with aryl ligand, (tBu)$_4$PcM (p-TMP) [M = Ga(III)(**3**), In(III)(**4**)], (**c**) phthalocyanine dimer linked by a oxygen atom with different metal atom in the central area, M = Ga(III)(**5**),In(III)(**6**) [9, 30]

value of the gallium phthalocyanines functionalized with the p-TMP group is reduced by a factor about 3.2 compared with chlorogallium phthalocyanine. (tBu)$_4$PcGa (p-TMP) with lower saturation energy density possesses of lower optical limiting threshold and exhibits better limiting property.

Blau and coworkers had prepared highly soluble phthalocyanine dimer [(tBu)$_4$PcM)$_2$O] (Fig. 3). The interaction between the oxygen atom and the central metal increased the excited singlet state lifetime [32]. Formation of oxygen axially bridged dimer suppressed the aggregation between the compounds. Thereby, phthalocyanine dimers **5** and **6** exhibited better optical limiting property than the monomers **1** and **2** [32].

The gallium phthalocyanines **1** and **5** have longer fluorescence lifetime (i.e., the lowest excited single state lifetime) than those of the indium phthalocyanines **2** and **6**. Comparison about fluorescence lifetimes between monomers and dimers reveals that the dimers have longer lifetime of the excited singlet state [11]. The dimers settle the aggregation problem effectively by axial substitution. To a certain extent, axial substitution in phthalocyanines enhances the optical limiting capability. The optical limiting ability exhibited by **5** and **6** in toluene at 532 nm laser pulse is better than the monomers **1**, **2** [32].

The dimers **5** and **6,** oxygen bridged axially metallophthalocyanine, have a weak (1 ± 2 nm) blue shift in the Q-band [33] and a red shift (1.5 nm) in the B-band. Exciton splitting resulting from the interaction between the oxygen atom and the central metal, gallium, or indium in the dimer is responsible for these phenomenons.

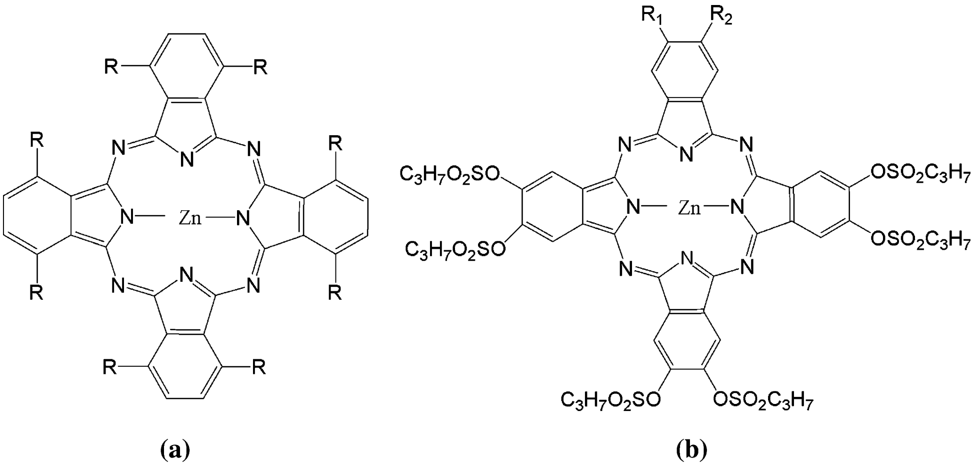
The optical limiting property of phthalocyanines with different substitution peripherally

A series of phthalocyanine monomers with same metal in the center cavity and varying macrocylce substituents peripherally are shown in Fig. 4. The optical limiting properties of these compounds, $(C_6H_{13})_8$PcZn, $(C_{10}H_{21})_8$PcZn, (iso-$C_5H_{11})_8$PcZn, $(OSO_2C_3H_7)_8$PcZn and $[(OSO_2C_3H_7)_6I]$PcZn, were all measured in their solution in toluene (1 g/L) [9]. Compounds **1** and **3** both exhibit larger value of nonlinear absorption coefficient, β_{I}, than the rest and the lowest β_{I} is hold by the compounds **4** and **5**. However, compound **4** possesses the smallest ratio of the absorption cross section, κ, and compound **5** has the largest value**.** The differences of κ among compounds **1**, **2**, **3**, and **5** are not large and the compound **5** has the largest absorption cross section. As far as saturation energy density F_{sta}, the compound **5** displays the largest magnitude followed closely by compound **4** and the smallest one is compound **3**. The value of F_{sta} shown by compound **1** is slightly larger than the compound **3**.

The substitution peripherally by alkyl groups is more beneficial to the improvement in optical limiting than other types of side groups. These compounds **1**, **2**, and **3** with alkyl groups also disperse the beam more effectively than the other two compounds **4** and **5** [9].

Optical limiting properties of carbon nanotubes

Recently, carbon nanotubes have emerged as a class of good materials for a broadband from visible to near



(a) **(b)**

Fig 4 Zinc phthalocyanine monomers with different peripheral substitution. (**a**) R = C_6H_{13}(**1**), $C_{10}H_{21}$(**2**), iso-C_5H_{11}(**3**), (**b**) R_1, R_2 = $-OSO_2C_3H_7$ (**4**), R_1 = $-OSO_2C_3H_7$,R_2 = I, (**5**) [9]

infrared in optical limiting applications. Optical limiting properties of both SWNT and MWNT carbon nanotubes have been explored [4, 5, 17, 34].

Nanotubes tend to aggregate into larger bundles because of high surface area. In some reports, the suspension of CNT is prepared in the presence of some surfactants [5, 19]. Recently, some groups reported stable suspension of carbon nanotubes can be received in amide solvents such as *N*,*N*-dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) after simple sonication and centrifugation processes [35, 36]. In addition, many works about functionalization of carbon nanotubes via covalent or noncovalent (π–π packing, etc.) with appropriate compounds have been done to improve their solubilization in organic solvents [7, 22, 37, 38]. For example, the soluble carbon nanotube was achieved by the combination of the nanotubes and highly soluble poly(propionylethylenimine-*co*-ethylenimine) or octadecylamine [18] and the homogeneous solutions were formed in chloroform at room temperature. The results reported showed that the suspended and solubilized carbon nanotubes were rather different in optical limiting response.

Optical limiting in SWNT suspensions

In order to increase the magnitudes in the suspension, carbon nanotubes are often dispersed in the solvent by addition of a surfactant. Riggs [18] reported that stable suspensions of full and shortened single-walled and MWNTs were prepared in water in the presence of a surfactant. Measurement of optical limiting properties for the suspension was conducted under 5 ns pulse width and 532-nm pulsed laser irradiation. Soluble carbon nanotube samples were achieved by the attachment of nanotubes to highly soluble poly(propionylethylenimine-*co*-ethylenimine) PPEI-EI, or by functionalizing the nanotubes with octadecylamine. The homogeneous solutions were formed in chloroform at room temperature. As a result, the carbon nanotubes samples exhibited weaker optical limiting responses in homogeneous solutions than in suspensions. These results agreed with the phenomenon reported by Liu [39]. He also found the optical limiting responses observed in MWNTS sample modified with didecylamine was weaker than those of MWNT suspension in chloroform after both samples were adjusted to 50% linear transmittance at 532 nm.

Both of the solvent in the suspension and pulse width have effects on the optical limiting response [39]. Carbon nanotubes in chloroform exhibit better limiting performance than in water [5, 19] and the threshold for the chloroform suspension is smaller than that for water suspension [5]. The differences in thermodynamic properties of chloroform and water are responsible for this phenomenon. Some values of the thermodynamic parameters of chloroform such as the heat conductivity, calorific capacity, boiling point, and vaporization energy of chloroform are all much smaller than those of water, which make it much easier for chloroform solvent molecules on the heating and vaporization that are involved in the main mechanism of nonlinear scattering. Mishra [17] reported optical limiting performance of SWNTs suspensions in water, ethanol, and ethylene glycol. The results exhibited that optical limiting in the ethanol suspension was the strongest in the three suspensions and the optical responses in ethylene glycol suspension were the lightest. The lowest threshold value was 1.0 J/cm^2 for the ethanol suspension. These observations suggested that the intensity of nonlinear scattering was related to the host liquid. They assigned the observed nonlinear scattering phenomenon to the formation of micro bubbles in the suspension. The strongest optical limiting behavior in the ethanol suspension was associated to its lowest boiling point among the three liquids, which agreed with Vivien's viewpoints [5].

Vivien also compared typical limiting curves for pulses of 5 and 80 ns in both water and chloroform suspension. The limiting threshold was significantly small at long pulse, 80 ns, for water and much smaller for chloroform [5]. Comparison on the optical limiting responses of MWNT in chloroform and *o*-dichlorobenzene (DCB) revealed that the limiting responses in $CHCl_3$ were slightly better than that in DCB [39] due to $CHCl_3$ with lower boiling point. In the graphic pictures illustrating vapor bubble formation in carbon nanotubes suspension in water and in chloroform [19], Vivien observed there were a small number of normal and big bubbles in water and many irregular and small bubbles in chloroform. These pictures confirmed that the integration of gaseous cavities was easier and effective in water than in chloroform. However, the chloroform suspension with many but smaller bubbles showed better nonlinear scattering ability because of more gaseous bubbles acting as scatting centers in suspension.

Jin et al. [40] prepared two kinds of samples: in the first sample, more than 60% of MWNTs had aspect ratios over 50, and in the other one, more than 80% of the MWNT had aspect ratios smaller than 50. The sample consisting of nanotubes with smaller aspect ratio was stable even subjected to large velocity centrifugation while the second sample comprised of nanotubes with larger aspect ratios formed deposition. This deposition could be dispersed in poly (vinylidene fluoride) (PVDF)/dimethylformamide (DMF) solution by sonication to produce a metastable colloidal system. Their experiments demonstrated that the sample with larger aspect ratios showed a stronger limiting effect than the other sample with smaller aspect ratios at low flounces (<1 J/cm^2). This fact could be explained by the nonlinear scattering model [40].

The effect of modification on the carbon nanotubes on optical limiting

Functionalized carbon nanotubes with tethered pyrenes

The samples were prepared by the esterification between carboxylic acids attaching to the surface of nanotubes and (3-decyloxy-5-pyrenyloxyphenylmethan1-ol) (**I_{py}**) or (3-decyloxy-5-pyrenyloxyphenylbutan-1-ol) (**I_{py}'**). These functionalized carbon nanotube samples **I_{py}**-SWNT, **I_{py}**-MWNT, and **I_{py}'**-SWNT [23], shown in Fig. 5, are all soluble in common organic solvents such as chloroform, THF, and toluene. Due to the addition of carbon nanotubes, the original absorption bands of **I_{py}** and **I_{py}'** in the 300–400 nm is somewhat red-shifted and become broader, which may be attributed to the configuration changes resulting from the functionalization on the nanotube surface [23]. The pyrene absorption in the UV/Vis absorption spectra is relatively stronger than the carbon nanotube absorption in the same wavelength region 300–400 nm while the carbon nanotube exhibits wider absorption at longer wavelengths [23, 41].

The functionalization on the nanotubes with pyrene combines their advantages and endows the composites with better absorption at wider bands. The excited-state energy absorbed by the pyrene is transferred to neighboring pyrene to form the pyrene excimer [23] and to nanotubes via intermolecular process [42]. These two competing quenching processes lead to the lower fluorescence quantum yield and faster decay of pyrene excimer emission. The difference in the fluorescence quantum yield of **I_{py}** and **I_{py}'** suggests that the branch length has effect on the excited-stated energy transfer and the shorter chain is favorable to the energy transfer. Shown by the absorption and fluorescence spectra of **I_{py}**-SWNT and **I_{py}**-MWNT in room temperature, the pyrene excimer has stronger emission intensity in **I_{py}**-SWNT than in **I_{py}**-MWNT. This might be attributed to SWNT with more flexible structure than MWNT which is benefit to the formation of pyrene excimer in the composites.

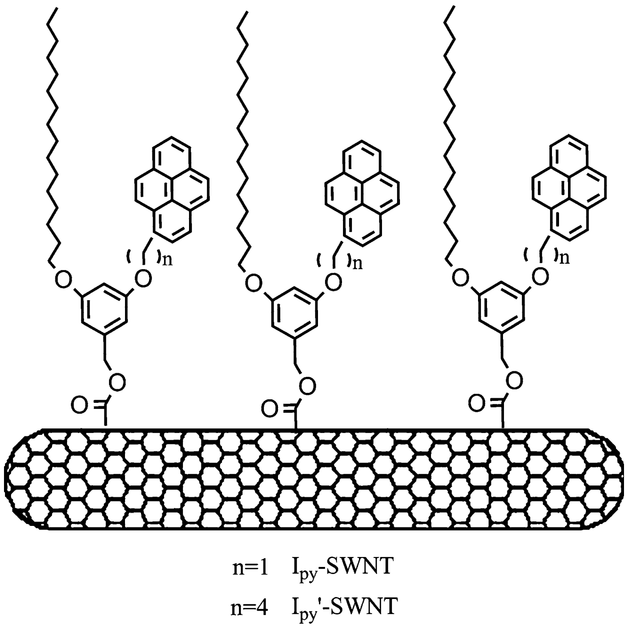
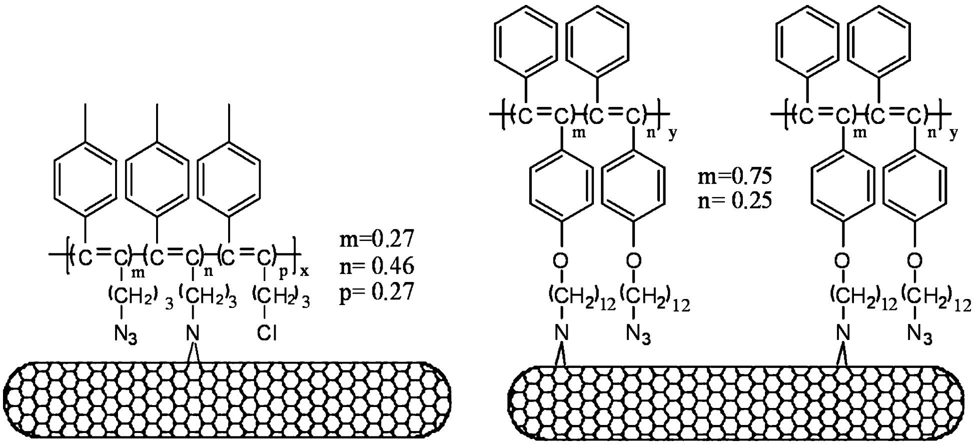


Fig. 5 The structure of carbon nanotubes composites, **I_{Py}**-SWNT, **I_{py}'**-SWNT [23]

Soluble SWNTs functionalized with polyacetylenes

SWNTs composite was prepared with conjugated polyacetylenes carrying halogen functional groups at the ends of their alkyl pendants. The chloro and bromo groups were substituted partly or completely by azido group and yielded the azido functionalized polymers, which were grafted to the SWNT through the cyclization reaction of the azido function with carbon nanotubes (shown in Fig. 6). Polymer chains wrap the carbon nanotubes sidewall [22]. The polyacetylene chains have little effect on the optical limiting property in the composite in addition to the improvement of the nanotubes solubility in common organic solvents. The optical limiting capability resulted mainly from the carbon nanotubes in the composite. Interestingly, the polymers and composites are luminescent under illumination of UV lamp.

Fig. 6 The structure of the composite consisting of nanotubes functionalized with polyacetylenes [22]



Xu [43] had prepared polyurethane–urea/MWNT composites by covalent linkage based on sol–gel process. The sample composites with various MWNT contents were homogeneous and transparent materials. There was no optical limiting behavior observed in the measurement of pure polyurethane-urea, so the optical limiting property in the sample arises from the MWNT. When the MWNT contents varied from 0.1 to 0.5%, the optical limiting threshold decreased from 0.4 to 0.2 J cm^{-2} [43]. This fact indicated that the transmittance decrease and much more transmitted energy will be limited with the MWNT mass increasing in samples.

Optical limiting property of composites prepared with carbon nanotubes and phthalocyanine or its derivatives

The composite of MWNTs linked covalently with copper phthalocyanine

Hatton [44] blended the soluble compound 3,4,4,4-tetrasulfonic acid tetrasodium salt copper phthalocyanine (TS-CuPc) (seen in Fig. 7) with surface-oxidized concentrated MWNTs (o-MWNTs) dispersions in water to form a stable nanocomposite solution. Copper phthalocyanine with macrocylce molecule configuration was linked to MWNT noncovalently through the π–π stacking function. The sample was made into film via spin coating on glass coated with indium-tin oxide (ITO) followed by rapid drying. The combination dynamic between the two components arise from a ground-state charge-transfer interaction with partial charge transfer from o-MWNT to TS-CuPc molecules.

In the UV/Vis absorption spectra, it was shown that the Q-band leak split originally into two leaks in the spectra of dilute aqueous solution of TS-CuPc, which were attributed to the monomer absorption and aggregation absorption arising from the formation of dimers or higher aggregates in the solution [45] and the absorption leak in the Q-band was dominated by one peak shown in the spectrum corresponding to film of the TS-CuPc.

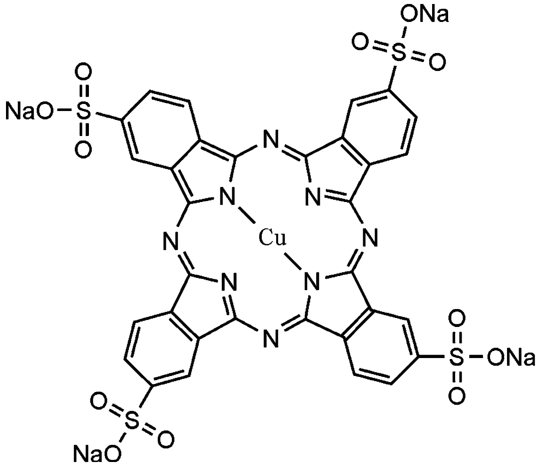


Fig. 7 The structure of the TS-CuPc [42]

The absorption of the nanocomposite film prepared with TS-CuPc and o-MWNTs covered the whole visible spectrum and was improved in some region due to the addition of TS-CuPc, for example, there was a broad absorption in Q-band (550–700 nm). The spectra of nanocomposite film consisted of the components inherent peaks which indicated the MWNT retained its original configuration [44].

Shown by the TEM image [44], the o-MWCNTs were fairly uniformly coated with TS-CuPc and the thickness of the coating layer was estimated to be 2–3 nm. They estimate that the plane of the macrocylce was parallel to the nanotube surface and stacked on the convex MWNT surface noncovalently in the structure of the composite of MWNT with TS-CuPc based on their test results.

SWNT functionalized with phthalocyanines

Ballesteros et al. [46] had prepared two new soluble hybrids of SWNTs functionalized with phthalocyanine

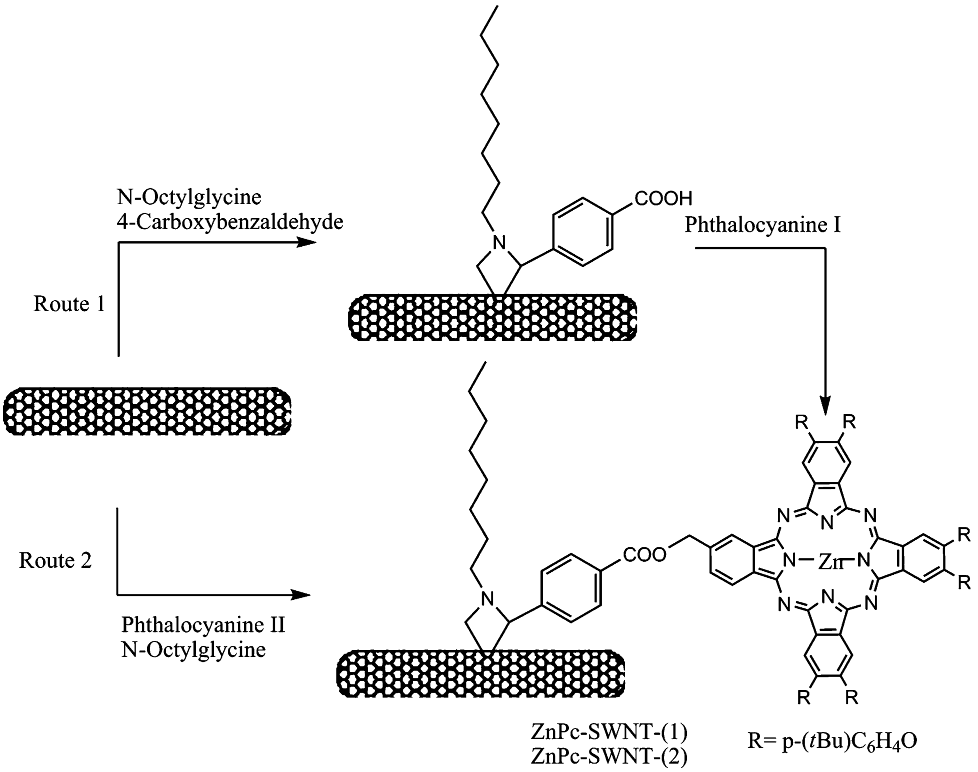


Fig. 8 The process of functionalization occurred on the sidewalls of SWNTs with phthalocyanine **I** and **II** to prepare ZnPc-SWNT-(1) and ZnPc-SWNT-(2) [46]

derivatives following two different routes, which are shown in Fig. 8.

The first route would involve a reaction of *N*-octylglycine and 4-formylbenzoic acid with SWNTs prior to esterification reaction between the functionalized SWNT and phthalocyanine derivative **I** (shown in Fig. 9) and this route yielded ZnPc-SWNT-(1). The second route, phthalocyanine derivative **II**, was added directly to the system and included *N*-octylglycine and SWNTs. The final product was ZnPc-SWNT-(2). The functionalized degrees in both routes were different and the former was higher.

In the Raman spectra, there were not enough evidences of any characteristic peak of the component included in the composites because of weak functionalization [46]. However, functionalization did bring about an improvement of the D-band [47–49] compared with pristine nanotube and the enhancing effect is larger for sample ZnPc-SWNT-(2). The estimated number of ZnPc units per carbon atom was quite small, which helped SWNTs to preserve the original electronic structure. The characteristic absorption intensity of SWNT in ZnPc-SWNT-(2) in the ground absorption spectra was stronger than ZnPc-SWNT-(1) due to lower degree of functionalization in ZnPc-SWNT-(2).

Composite film consisted of naphthalocyanine and carbon nanotube

The composite of carbon nanotube functionalized with naphthalocyanine (NaPc-MWNT) was prepared by π–π packing and was dissolved in chloroform [50]. The

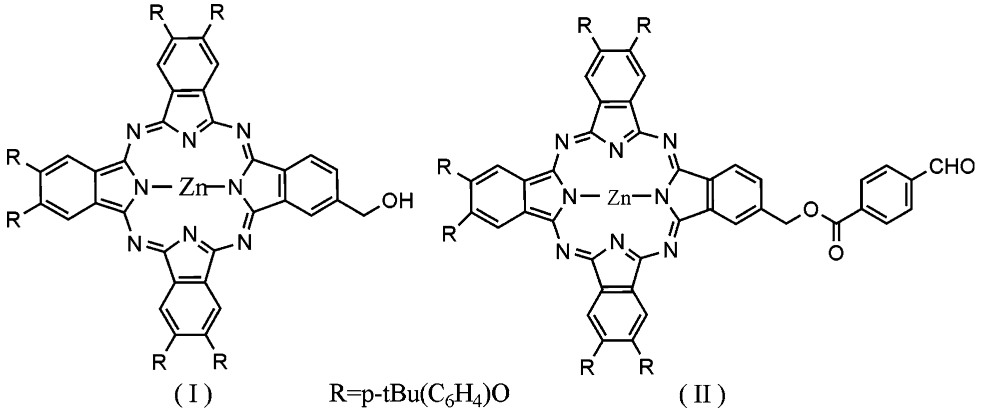


Fig. 9 The structure of the phthalocyanines derivative **I** and **II** [46]

nanocomposite was made into film by spin coating the solution of NaPc-MWNT in chloroform on a glass substrate coated with indium-tin oxide (ITO). Furthermore, poly(3-hexylthiophene)(PAT6) was added into the chloroform solution and achieved another composite with three components, NaPc-MWNT-PAT6. The latter composite was also made into film in the same way. The NaPc-MWNT solution in the UV/Vis absorption spectra at room temperature exhibit strong absorption bands from 250 to 350 in the ultraviolet region with a weak decaying tail covering the whole visible region and around 700 nm in the near-infrared region [50]. Compared with the absorption of nanotube in UV/Vis absorption [28, 39], the addition of NaPc improves distinctly the absorption of carbon nanotube in the ultraviolet and near-infrared region and strengthens the optical limiting response of SWNTs, which is indicated by broadening Q-band and red-shift. The broadening Q-band and red-shift observed in the spectra of the NaPc–MWNT film is attributed to intermolecular π–π electronic interaction arising from π–π stacking in the solid state. But the absorptive intensity in the spectra of film corresponding to NaPc–MWNT, NaPc-PAT6, and PAT6, respectively, on the ITO glass did not increase obviously. With respect to spectrum of the NaPc-MWNT-PAT6 film, the spectra exhibited unexpectedly extensive and strong absorption ranges from near-ultraviolet, visible to near-infrared wavelength band ranges and the absorption baselines are raised [50]. Further studies are needed to give rational explanation for this phenomenon.

Conclusion

In this review, we introduce simple optical limiting property of phthalocyanines, their derivatives, and carbon nanotubes and some routes to change their limiting ability. Besides, the mechanisms of nonlinear optical limiting are also reviewed, for example, nonlinear absorption, nonlinear scattering, and nonlinear refraction. Phthalocyanines with extensive two-dimensional π-electron system are a potential optical limiting material. Substitution peripherally or axially can improve obviously phthalocyanines and its derivatives in optical limiting effect. On the other hand, some heavy metal atoms can be inserted into the centre area to meliorate their limiting abilities. Carbon nanotubes exhibit broad absorption in the UV/Vis absorption spectra. Because of its inferior solubility in common organic solute, much work has been done to increase the solubility of nanotube through sorts of modification on carbon nanotubes. The composites prepared with carbon nanotubes and phthalocyanine or its derivatives exhibit favorable optical limiting property. Combination of carbon nanotubes and phthalocyanines is a promising path to prepare better optical limiting devices.

So far, many phthalocyanine derivatives and composites consisting of carbon nanotubes and phthalocyanine derivatives have been prepared and their optical limiting parameters are also discussed. However, it is necessary to devote much more detailed work to the researches about factors affecting optical limiting responses and summarize some regular conclusions about the relations between the structure and optical limiting effect to direct the preparation of desirable materials. In addition, the optical limiting principles involved in phthalocyanine derivatives, especially the composites comprised of carbon nanotubes and phthalocyanine derivatives, have not been interpreted clearly. Practical optical limiter prepared with phthalocyanines or the composites contained phthalocyanines and carbon nanotubes will involve integrating the phthalocyanines or the composites into some solid state mediums. But present studies about them are generally focused on the performances in solution state. So, further work is needed to realize the practical use in this field.

The research of our work is focus on the preparation of solid state optical limiting materials contained composites consisting of phthalocyanines and carbon nanotubes through sol–gel method. Now, we have prepared the composites through π–π stacking route on the beginning of the work and the next work about preparing solid materials contained composites by sol–gel method is going according to the plan.

References

1. Wu B, Zhang C, Zhang W (2005) Organic-inorganic hybrid materials and application (Chinese), 1st edn. Chemical Industry Press, Beijing
2. O'Flaherty SM, Murphy R, Hold SV, Cadek M, Coleman JN, Blau WJ (2003) J Phys Chem B 107:958. doi:10.1021/jp0271108
3. Fu S, Zhu X, Zhou G, Wong W-Y, Ye C, Wong W-K et al (2007) Eur J Inorg Chem 2004. doi:10.1002/ejic.200601190
4. Huili S, Aizhi L (2004) Technol Econ Areas Commun (Chinese) 1:51
5. Vivien L, Izard N, Riehl D, Hache F, Anglaret E (2003) AIP Conf Proc 685:559. doi:10.1063/1.1628093
6. Liu Z, Tian J-G, Guo Z, Ren D-M, Du F, Zheng J-Y et al (2008) Adv Mater 20:511. doi:10.1002/adma.200702547
7. Sun X, Yu RQ, Xu GQ, Hor TSA, Jia W (1998) Appl Phys Lett 73(25):3632. doi:10.1063/1.122845
8. Slodek A, Wöhrle D, Doyle JJ, Blau W (2006) Macromol Symp 235:9. doi:10.1002/masy.200650302
9. O'Flaherty SM, Hold SV, Cook MJ, Torres T, Chen Y, Hanack M, Blau WJ (2003) Adv Mater 15:19
10. Cheng F, Alex A (2006) Chem Eur J 12:5053. doi:10.1002/chem.200600302
11. Chen Y, Hanack M, O'Flaherty S, Bernd G, Zeug A, Roeder B et al (2003) Macromolecules 36:3786. doi:10.1021/ma025939e
12. Shirk JS, Pong RGS, Flom SR, Heckmann H, Hanack M (2000) J Phys Chem A 104:1438
13. Hanack M, Schneider T, Barthel M, Shirk JS, Flom SR, Pong RGS (2001) Coord Chem Rev 219–221:235. doi:10.1016/S0010-8545(01)00327-7

14. Dini D, Barthel M, Hanack M (2001) Eur J Org Chem 3759–3769. doi:10.1002/1099-0690(200110)2001:20<3759::AID-EJOC3759>3.0.CO;2-U
15. Chen P, Wu X, Sun X, Lin J, Ji W, Tan KL (1999) Phys Rev Lett 82(12):2548. doi:10.1103/PhysRevLett.82.2548
16. Wang J, Blau WJ (2008) J Phys Chem C 112:2298. doi:10.1021/jp709926r
17. Mishra SR, Rawat HS, Mehendale SC, Rustagi KC, Sood AK, Bandyopadhyay R, Govindaraj A, Rao CNR (2000) Chem Phys Lett 317:510. doi:10.1016/S0009-2614(99)01304-4
18. Riggs JE, Walker DB, Carroll DL, Sun Y-P (2000) J Phys Chem B 104:7071. doi:10.1021/jp0011591
19. Viviena L, Riehla D, Hacheb F, Anglaret E (2002) Physica B 323:233. doi:10.1016/S0921-4526(02)00974-2
20. Vivien L, Anglaret E, Riehl D, Hache F, Bacou F, Andrieux M et al (2000) Opt Commun 174:271. doi:10.1016/S0030-4018(99)00656-2
21. Nashold KM, Walter DP (1995) J Opt Soc Am B 12:1228
22. Li Z, Dong Y, Halussler M, Lam JWY, Dong Y, Wu L, Wong KS, Tang BZ (2006) J Phys Chem B 110:2302. doi:10.1021/jp056413+
23. Martin RB, Qu L, Lin Y, Harruff BA, Bunker CE, Gord JR et al (2004) J Phys Chem B 108:11447
24. Jin Z, Sun X, Xu G, Goh SH, Ji W (2000) Chem Phys Lett 318:505. doi:10.1016/S0009-2614(00)00091-9
25. Banerjee S, Hemraj-Benny T, Wong SS (2005) Adv Mater 17(1):6424. doi:10.1002/adma.200401340
26. Tang BZ, Xu H (1999) Macromolecules 32:2569. doi:10.1021/ma981825k
27. Chitta R, Sandanayaka ASD, Schumacher AL, D'Souza L, Araki Y, Ito O et al (2007) J Phys Chem C 111:6947. doi:10.1021/jp0704416
28. Cao L, Chen H, Wang M, Sun J, Zhang X, Kong F (2002) J Phys Chem B 106:8971. doi:10.1021/jp020680n
29. Li H, Martin RB, Harruff BA, Carino RA, Allard LF, Sun Y-P (2004) Adv Mater 16(11):896. doi:10.1002/adma.200306288
30. de la Torre G, Va'zquez P, Agulló-López F, Torres T (2004) Chem Rev 104:3723. doi:10.1021/cr030206t
31. Perry JW, Mansour K, Marder SR, Perry KJ, Alvarez D Jr, Choong I (1994) Opt Lett 19:625
32. Chen Y, Subramanian LR, Fujitsuka M, Ito O, O'Flaherty S, Blau WJ, Schneider T, Dini D, Hanack M (2002) Chem Eur J 8(18):4248. doi:10.1002/1521-3765(20020916)8:18<4248::AID-CHEM4248>3.0.CO;2-R
33. Manas ES, Spano FC, Chen LX (1997) J Chem Phys 107(3):707. doi:10.1063/1.474436
34. Krivokapic A, Anderson HL, Bourhill G, Ives R, Clark S, McEwan KJ (2001) Adv Mater 13(9):652. doi:10.1002/1521-4095(200105)13:9<652::AID-ADMA652>3.0.CO;2-3
35. Wang J, Blau WJ (2008) J Phys Chem C 112:2298
36. Giordani S, Bergin SD, Nicolosi V, Lebedkin S, Kappes MM, Blau WJ, Coleman JN (2006) J Phys Chem B 110:15708
37. Balasubramanian K, Burghard M (2005) Small 1(2):180. doi:10.1002/smll.200400118
38. Zang L, Liu C, Li Q, Wang Z, Liu Z, Gong Q (2006) Opt Commun 265:354
39. Luqi L, Zhang S, Qin Y, Guo Z-X, Ye C, Zhu D (2003) Synth Met 135–136:853
40. Jin Z, Huang L, Goh SH, Xu G, Ji W (2002) Chem Phys Lett 352:328
41. Angeles Herranz M, Ehli C, Campidelli S, Gutiérrez M, Hug GL, Ohkubo K, Fukuzumi S, Prato M, Martin N, Guldi DM (2008) J Am Chem Soc 130:66
42. Martin RB, Fu K, Sun Y-P (2003) Chem Phys Lett 375:619
43. Xu M, Zhang T, Gu B, Wu J, Chen Q (2006) Macromolecules 39:3540
44. Hatton RA, Blanchard NP, Stolojan V, Miller AJ, Ravi S, Silva P (2007) Langmuir 23:6424
45. Camp PJ, Jones AC, Neely RK, Speirs NM (2002) J Phys Chem A 106:10725
46. Ballesteros B, de la Torre G, Ehli C, Aminur Rahman GM, Agulló-Rueda F, Guldi DM, Torres T (2007) J Am Chem Soc 129:5061
47. Menard-Moyon C, Izard N, Doris E, Mioskowski C (2006) J Am Chem Soc 128:6552
48. Chiu PW, Duesberg GS, Dettlaff-Weglikowska U, Roth S (2002) Appl Phys Lett 80(20):3811
49. Dyke CA, Tour JM (2004) Chem Eur J 10:812
50. Feng W, Li Y, Feng Y, Wu J (2006) Nanotechnology 17:3274