Broadband optical limiting optimisation by combination of carbon nanotubes and two-photon absorbing chromophores in liquids

Didier Riehl, Nicolas Izard, Laurent Vivien, Eric Anglaret, Eric Doris, Cécilia Ménard, Charles Mioskowski, Louis Porrès, Olivier Mongin, Marina Charlot, et al.

Broadband optical limiting optimisation by combination of carbon nanotubes and two-photon absorbing chromophores in liquids

D. Riehl[*a], N. Izard [a,b] , L. Vivien [a], E. Anglaret [b],
E. Doris [c], C. Ménard [c], C. Mioskowski [c],
L. Porrès [d], O. Mongin [d], M. Charlot [d], M. Blanchard-Desce [d],
R. Anémian [e], J.-C. Mulatier [e], C. Barsu [e], C. Andraud [e]
[a] Délégation Générale pour l'Armement – Centre Technique d'Arcueil, Arcueil, France
[b] Université Montpellier II – Groupe de Dynamique des Phases Condensées, Montpellier, France
[c] Commissariat à l'Energie Atomique – Service des Molécules Marquées, Gif-sur-Yvette, France
[d] Université Rennes I – Synthèse et Electrosynthèse Organiques, Rennes, France
[e] Ecole Normale Supérieure de Lyon – Stéréochimie et Interactions Moléculaires, Lyon, France

ABSTRACT

Nowadays, it seems evident that a unique nonlinear optical (NLO) material cannot offer simultaneously linear transparency, colour neutrality and broadband optical limiting efficiency at the performance levels required for sensor and eye protection against all laser threats. Several combinations of NLO materials were investigated last few years, including multicell or multilayer geometries.

The approach presented here combines multiphoton absorption with nonlinear scattering. For that purpose, singlewall carbon nanotubes are suspended in various solutions of multiphoton absorbing chromophores. Such combinations allow us to obtain optical limiters of high linear transmittance and excellent colour neutrality. Broadband optical limiting is expected from the association of these two broadband materials, and enhanced optical limiting efficiency is expected from cumulative effects in the nanosecond regime.

We report here on the optical limiting studies performed with nanosecond laser pulses on several families of multiphoton absorbers in chloroform, with carbon nanotubes suspended in the solutions. The performances of these samples are compared with those of simple multiphoton absorber solutions and carbon nanotube suspensions, and the differences observed are interpreted in terms of cumulative NLO effects and adverse aggregation phenomenon. Ways to optimise stability of the suspensions are also experimented and discussed.

Keywords : optical limiting, carbon nanotube, nonlinear scattering, multiphoton absorption.

1 . INTRODUCTION

1 . 1 Materials for optical limiting

For protection of the eye observing through optical sighting systems, an ideal optical limiter (placed at an intermediate focal plane of such an optical system) should exhibit broadband optical limiting **(OL)** efficiency (on the whole visual spectrum, and eventually in the near infrared too). Moreover, OL properties should be effective on a broad range of laser exposure durations and repetition rates, i.e. from the sub nanosecond pulsed regime to the continuous regime, and from the single shot mode to high repetition rate pulse trains. In addition, the limiter should preserve observation's ergonomics through high linear optical transmittance and neutral colourimetry.

Eye protection against pulsed laser threat has motivated an intense research effort during the last fifteen years, leading to the emergence of three classes of nonlinear optical **(NLO)** materials showing interesting potentialities for that application: reverse saturable absorbers **(RSA)**, multiphoton absorbers **(MPA)** and nonlinear scattering **(NLS)** materials.

[*] Didier.Riehl@etca.fr

Reverse saturable absorbing molecules [1-18] have shown very efficient OL properties, either in solution or in a solid matrix (xerogel [11-14] or polymer [15-18]). In particular, porphyrins and derivatives [1-7] (phthalocyanines, naphthalocyanines) and some other classes of chromophores exhibit dramatically enhanced OL performance when incorporating a heavy metal atom (Pb, Au, Ag, Pt, Pd). Fullerenes [8-10] (C_{60} and C_{70}, chemically modified or not) also give valuable OL performance. Very low OL thresholds (as low as a few mJ/cm^2 in the ns regime) and strong laser attenuation can be obtained from the subpicosecond to the microsecond pulse regime, but only on a relatively narrow spectral band. Moreover, RSA behaviour is initiated by one-photon absorption of the ground state, which means that RSA materials exhibit strong coloration. Broadband OL efficiency and acceptable colour neutrality can be achieved by mixing several molecules, but only with a drastic reduction of linear transmittance.

By contrast, multiphoton absorbers in solution [19-26], solid matrix or in organic crystals [27] generally exhibit high linear transmittance and a more favourable colourimetry (from yellowish to colourless), the principal ground state absorption bands being located in the UV region. Instantaneous two-photon singlet-singlet excitation is responsible of the OL behaviour in ps and sub-ps regimes. However, sequential three-photon absorption process (two-photon absorption followed by single-photon excited state absorption) preserve OL performance for pulse duration up to a few nanoseconds.

Nonlinear scattering materials consist principally in suspensions of absorbing nanoparticles [28-38] in organic solvents. Under laser irradiation, heating of the particles causes evaporation of the surrounding solvent and sublimation of the particles themselves, leading to fast growth of strongly scattering gaseous cavities. The response time of NLS is of the order of one nanosecond, with high OL efficiency in the ns and µs regimes. Good results were obtained with carbon black suspensions **(CBS)** [28-33] and, more recently, with carbon nanotube suspensions [34-37]: broadband OL efficiency was demonstrated on the whole visible-near IR spectral range, with excellent colourimetry and high linear transmittance (carbon concentration in the suspensions ranges from a few to a few tens of mg/l).

1 . 2 Multi-material approach

It is obvious that none of these NLO materials fulfil all the requirements of OL application in terms of colourimetry, linear transmittance, and broadband OL efficiency for all pulse lengths. However, adequate response to a wider variety of laser threats can be obtained by combination of several complementary NLO materials. Cascaded geometries [38-43] (tandem/multicell configurations [38-41] for liquids limiters, multilayer [42-43] for solids) allow a considerable increase of damage thresholds but present a major drawback: only one element is located at the intermediate focal plane of the optical sighting system, thus OL performance improvement is weak because of the extra focal locations of the other elements. An interesting alternative was proposed recently [44], using two intermediate focal planes with a carbon bisulfide cell at the first and a CBS cell at the second. Broadband OL performance and damage thresholds were greatly enhanced, however the integration in a real sighting system becomes problematic due to the need for two intermediate focal planes and additional field lenses.

These considerations led us to follow another way, consisting in the combination of two different nonlinear materials in a single cell. We have chosen to combine nonlinear scattering with multiphoton absorption, by means of suspending singlewall carbon nanotubes **(SWNT)** in MPA solutions. From the cumulated contributions of these two complementary NLO materials we expect: broadband OL behaviour from the sub picosecond to the microsecond pulse regimes, good colour neutrality, high linear transmittance, and significantly enhanced OL performance in the nanosecond regime by cumulative contributions of MPA and NLS.

2 . PRELIMINARY RESULTS : SWNT/MPA IN WATER

2 . 1 Sample preparation, experimental set-up

Singlewall carbon nanotubes, synthesised by the electric arc discharge technique, were purchased from Nanoledge. They were characterised by X-ray diffraction, transmission and scanning electronic microscopy and by Raman spectroscopy : SWNTs of (1.3 ± 0.2) nm diameter are arranged in nanocrystalline bundles of 15-20 nm diameter. SWNTs are dispersed in water-containing 2-mm internal pathlength fused silica cells, with a small amount (1% by weight) of SDS surfactant in order to ensure stability of the suspensions. SWNT concentration was adjusted to obtain a linear transmittance of approximately 70% at 532 nm wavelength.

The reference molecule for multiphoton absorption is the commercially-available stilbene-3 [23], depicted in Fig.1. Stilbene-3 is generally used in DMSO because of his high solubility (up to 300 g/l) in this solvent but, due to the presence of sulfonate radicals, stilbene-3 exhibits poor solubility in water. The stilbene-3 concentration was only 20 g/l in our water solution. The composite (SWNT+stilbene-3)/water was obtained by simply adding stilbene-3 in a water suspension of carbon nanotubes, the SWNT and MPA concentrations being the same as those of the « simple » samples.

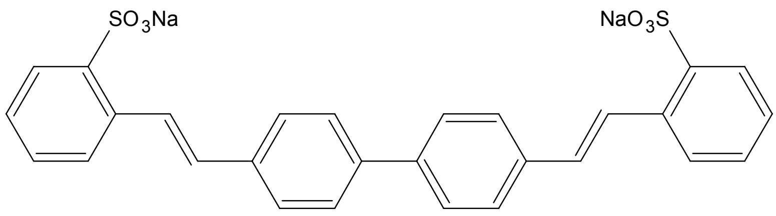
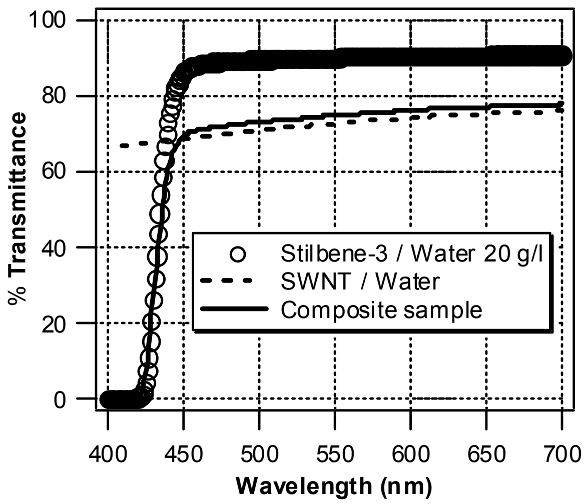


Figure 1 : chemical structure of stilbene-3

Transmittance spectra were recorded using a Cary-5 spectrophotometer. Nonlinear transmittance measurements were performed using frequency-doubled Nd :YAG pulses of 7 ns FWHM duration at 532 nm, on a classical RSG19 experimental test bed (uniform entrance pupil irradiation, F/5 focusing geometry).

2 . 2 Results



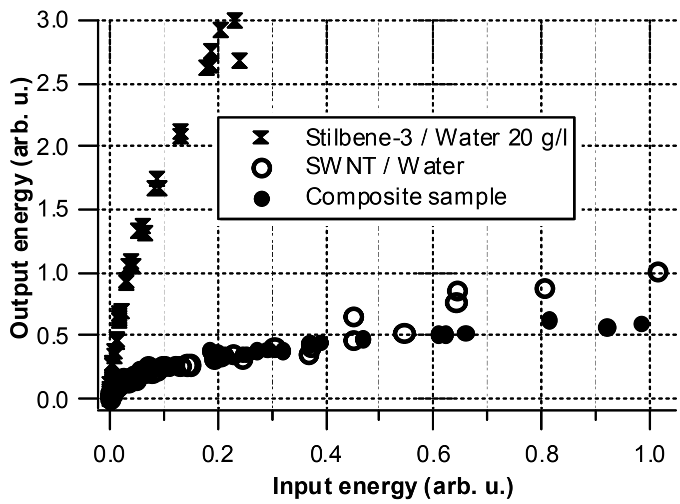


Figure 2 : transmission spectra of water samples (stilbene-3 at 20 g/l, carbon nanotube suspension and composite sample).

Figure 3 : optical limiting performance of water samples (RSG19, F/5, 532 nm, 7-ns).

Figure 2 shows the linear transmittance spectra of the three samples. As expected, the stilbene-3 sample exhibits high transparency and good colourimetry (cut-off wavelength around 420 nm, very pale yellow colour), and the carbon nanotube sample is totally colourless. In terms of linear properties, the composite sample is very satisfying, weakly coloured and with a photopic transmittance above 70%.

The optical limiting results are shown on Fig.3. The low-concentrated stilbene-3 solution is a poor performer compared to the SWNT suspension, the maximum output energy being approximately four times larger. However, the contribution of stilbene-3 molecules is visible on the limiting curve of the composite sample, which shows a maximum output energy 40% lower than that obtained with the carbon nanotube suspension. These encouraging results should be improved by using a best-suited solvent (most favourable to the growth of scattering centres in SWNT suspensions) and highly soluble MPA chromophores.

3 . CHLOROFORM SAMPLES

3 . 1 Carbon nanotube suspensions

The physical mechanisms responsible of the nonlinear scattering behaviour and the effect of solvent were extensively studied in carbon black and carbon nanotube suspensions. Four distinct mechanisms can be distinguished :

i.) Thermal transfer from the particles to the solvent induces formation of solvent bubbles [30-32, 45, 46]. For carbon nanotubes suspended in chloroform, the fluence threshold for that mechanism is as low as 2 mJ/cm^2. Due to the relatively slow growth of solvent bubbles, the OL threshold decreases with pulse duration : approximately 80-100 mJ/cm^2 for 3 ns pulses, 20 mJ/cm^2 for 15 ns pulses and 2 mJ/cm^2 for 50 ns pulses.

ii.) Intense heating of the particles leads to their sublimation, followed by explosive growth of hot carbon vapour cavities [30-33, 46-50]. The response time of that effect is approximately 1 ns, the sublimation threshold of 80-100 mJ/cm^2 (being also the limitation threshold for pulse duration less than 5 ns) is independent of pulse duration in the nanosecond regime.

iii.) At higher incident fluences, ionisation occurs, leading to the growth of absorbing microplasmas [28, 29, 47]. Some debates remain on the threshold of that effect, which is difficult to discriminate from the simple sublimation process.

iv.) At high incident fluences (several tens of J/cm^2 in the ns regime) breakdown of the whole focal volume contributes strongly to optical limiting, as for all-types liquid optical limiters.

It has also been shown that solvents possessing low specific heat, thermal conductivity, surface tension, boiling temperature and enthalpy of vaporisation permit lower OL thresholds and significantly better OL efficiency than water [30-32, 46]. Solvent effect is more noticeable for longer pulses.

The solvent effect is illustrated in Fig.4, which shows optical limiting performances obtained on RSG19 test bed (532 nm, 7 ns) with carbon nanotubes suspended in water and in chloroform at identical carbon concentrations. Maximum output energy is reduced by a factor larger than six in the SWNT/chloroform suspension. That result shows clearly the interest of combining highly soluble MPA chromophores with SWNTs in chloroform. However, the stability of the carbon nanotube suspensions in chloroform is less satisfying than that of SWNT/water suspensions : aggregation of carbon nanotubes occurs within a few weeks. Even if this aggregation is reversible (a few minutes of sonication are sufficient to disperse the samples), stability remains an open challenge.

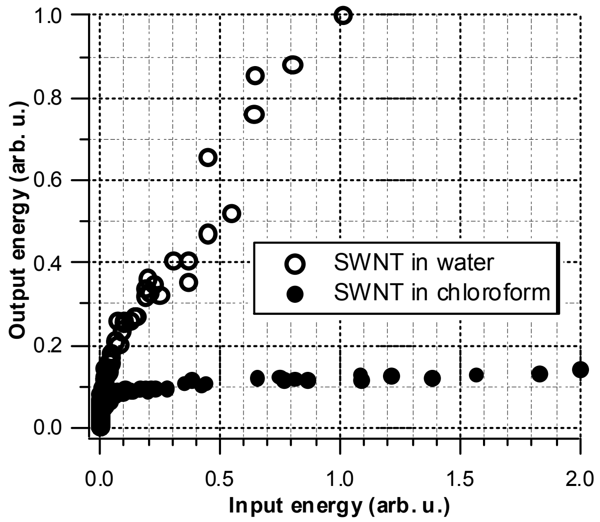


Figure 4 : effect of the solvent on optical limiting performance of carbon nanotube suspensions (RSG19, f/5, 532 nm, 7 ns, same energy scaling as on Fig.3.

3 . 2 Solubilisation of stilbene-3 in chloroform. New MPA chromophores

In order to solubilise stilbene-3 in chloroform, its chemical structure was slightly modified, at the group of Commissariat à l'Energie Atomique. The chemical structure is shown on Fig.5 : the modification consisted in the substitution of the Na$^+$ ion by an ammonium salt. High solubility in chloroform (> 200 g/l) is ensured by the two $C_{18}H_{37}$ chains.

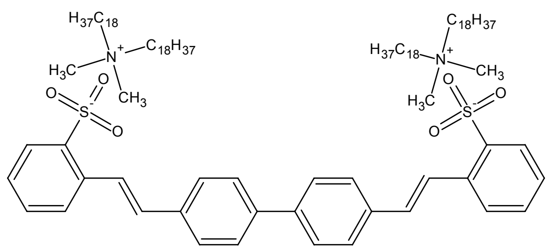
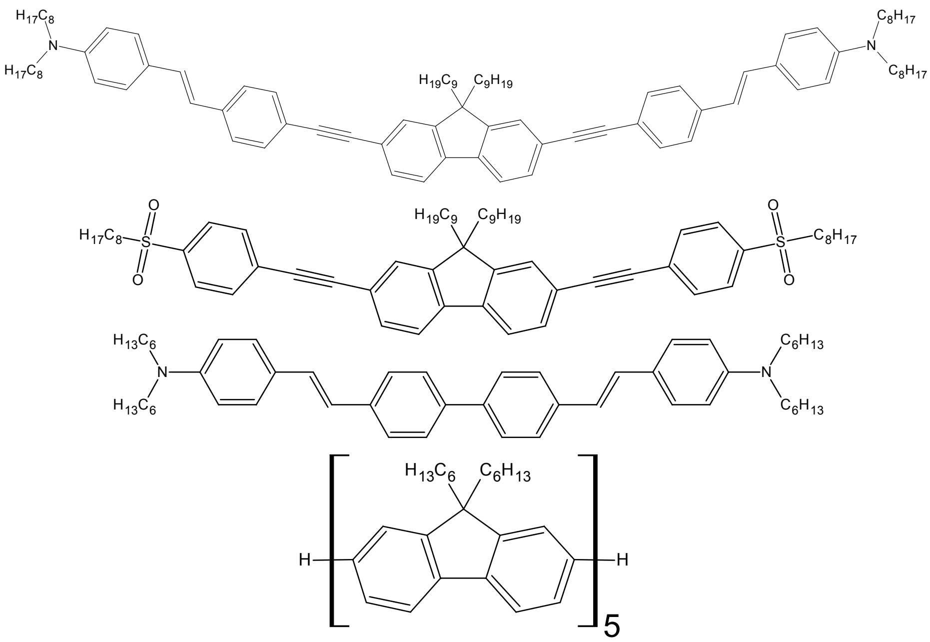


Figure 5 : chemical structure of modified stilbene-3 **(MST)**.

Carbon nanotubes were also combined with a wide variety of new MPA chromophores. Figure 6 shows chemical structures of some of these chromophores. RC1 [51], RC2 and RC3 [52], synthesised at University of Rennes, are built from the grafting of elongated conjugated rods bearing donor or acceptor end groups onto a conjugated core (fluorene for RC1 and RC2, biphenyl for RC3). The fluorene oligomer penta(dihexyl-fluorene) (PDHF) [53] was synthesized at Ecole Normale Supérieure de Lyon.



RC1

RC2

RC3

PDHF

Figure 6 : chemical structures of MPA chromophores synthesised at Rennes and at Lyon.

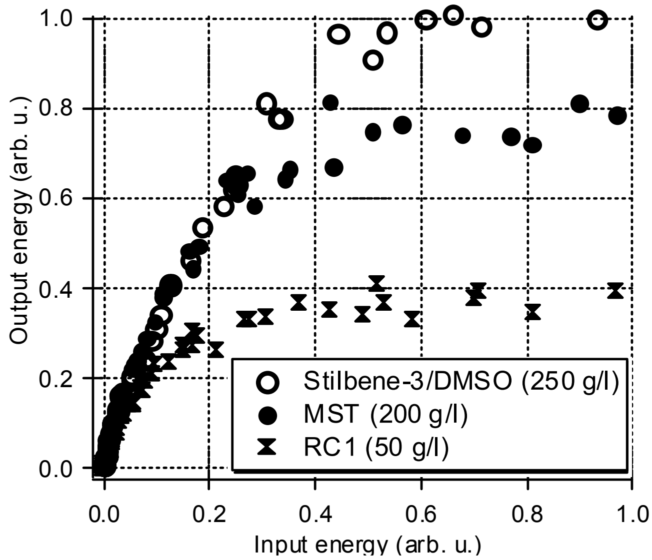
The linear properties of MPA chromophores are summarised in Table 1. Due to the small quantities available, concentrations of RC1-3 and PDHF were adjusted to 50g/l in the chloroform solutions and in the mixtures.

	Stilbene-3 (DMSO)	**MST**	**RC1**	**RC2**	**RC3**	**PDHF**
λ cut-off (nm)	420	415	485	425	475	420
Concentration (g/l)	250	200	50	50	50	50
Colour	Very pale yellow	Colourless	Lemon yellow	Pale yellow	Lemon yellow	Very pale yellow

Table 1 : Linear properties of MPA solutions.

In addition to RSG19 experiments (F/5, 532 nm, 7 ns), nonlinear transmittance measurements were also performed with other experimental set-up employing laser sources of different pulse durations. The first arrangement employed an optical parametric oscillator (OPO) emitting 3 ns pulses, and a Q-switched (non injected) frequency-doubled Nd :YAG laser, emitting 15 ns pulses, was used for the second. Long-focus geometries were used, with confocal lengths significantly longer than cell pathlengths : OPO and Nd :YAG operated at F/30 and F/50, respectively.

Results are given on Fig.7, for three different pulse durations. Chromophore concentrations are 250 g/l for the stilbene-3/DMSO reference sample, 200 g/l for STM/chloroform, and 50 g/l for all others in chloroform. The chemical modification of stilbene-3 does not induce negative effects on its NLO behaviour, at least at 532 nm, as shown by Fig.7a : in spite of lower molar concentration, OL performance of the MST/chloroform sample is slightly better than that of the stilbene-3/DMSO solution.



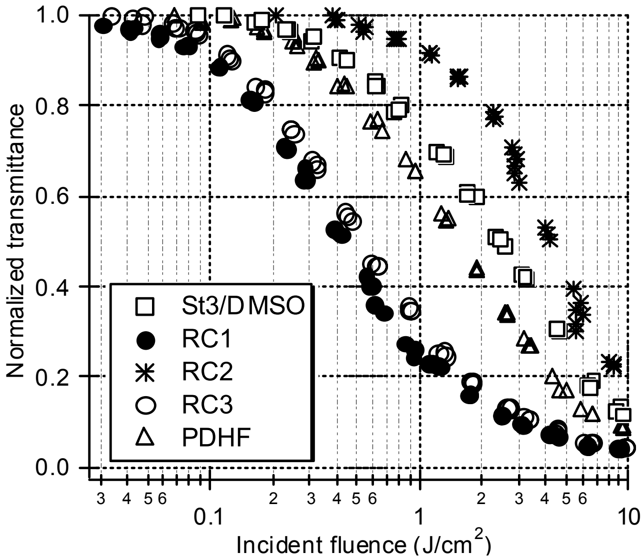
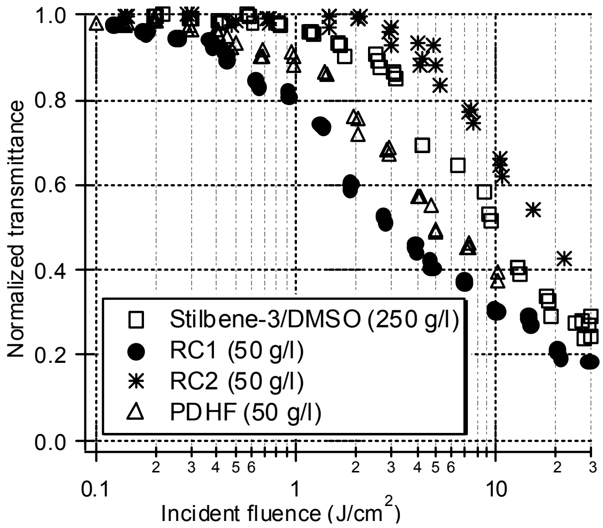


Figure 7 : optical limiting of multiphoton absorbers at 532 nm wavelength.

a) (Upper left) : RSG19, F/5, 7 ns.
b) (Upper right) : F/30, 3 ns (OPO).
c) (Bottom right) : F/50, 15 ns (Nd :YAG).



RC1, RC3 and PDHF solutions, even at a concentration as low as 50 g/l, are more efficient than the stilbene-3/DMSO reference sample. RC1 and RC3 solutions exhibit excellent OL performances, having limiting thresholds well below $1 J/cm^2$ even with 15 ns pulses, but with a distinct yellow colour (cf. Table 1). PDHF performs not as well as RC1 and RC3 but significantly better than Stilbene-3, particularly with 15 ns pulses (maybe due to a longer excited-state lifetime), and with a quasi-neutral colourimetry.

3 . 3 SWNT/MPA combinations

SWNT/MPA combinations in chloroform were prepared as in water. In a few days or weeks (depending on the MPA chromophore) after elaboration of the samples, an intriguing phenomenon was observed : aggregation occurred faster than in simple SWNT suspensions, but the effect was different. In SWNT suspensions, aggregation leads to precipitation of SWNTs in the bottom of the cells. In SWNT/MPA samples flocculation occurs faster, and the flocculates remain in suspension. The phenomenon is easily reversible by simple shaking. A possible explanation consists in the pi-stacking of the aromatic rings of the MPA chromophores on the surface of carbon nanotube bundles, such an effect being favoured by the plane structures of MPA chromophores.

The first nonlinear transmittance measurements, performed on RSG19 test bed, give some useful information. The results, shown in Fig.8, are at first sight particularly disappointing : the performances of SWNT/MPA samples are significantly lower than that of the SWNT suspension. Even the less efficient chromophores, like RC2, seem to strongly penalise SWNT OL efficiency.

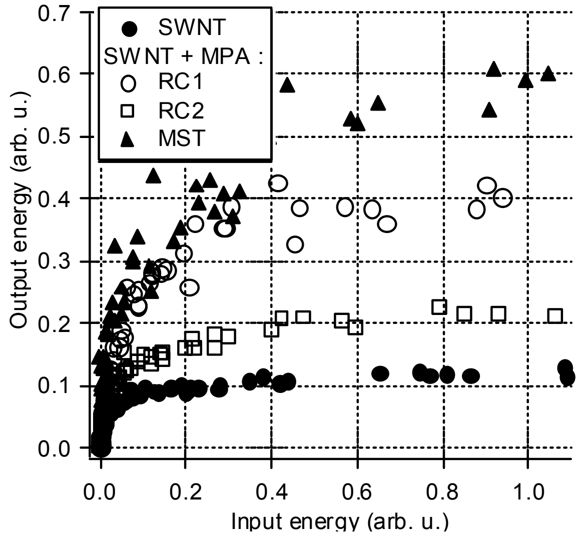


Figure 8 : optical limiting of SWNT suspension and of SWNT/MPA composites in chloroform (RSG19, F/5, 532 nm, 7 ns). The energy scaling is the same as on figures 3 and 4.

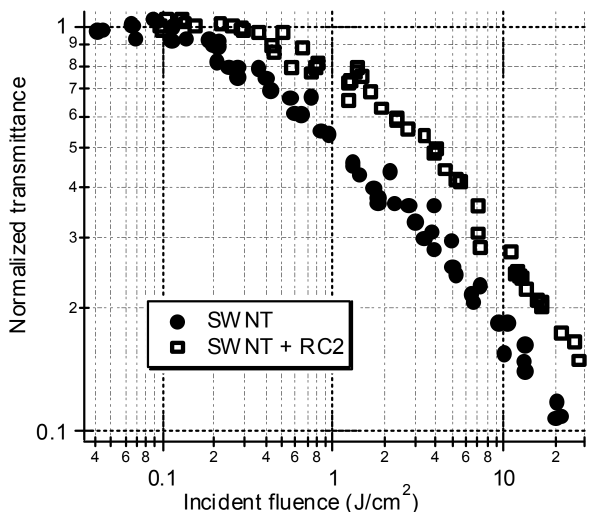


Figure 9 : normalised transmittance of SWNT suspension and SWNT/RC2 composite Vs incident fluence (RSG19, F/5, 532 nm, 7 ns).

Figure 9 compares the nonlinear transmittances of SWNT and SWNT/RC2 composite at low to moderate incident fluences. It is remarkable that OL performance of the composite is penalised well below the limiting threshold of the RC2 solution, which is above 1 J/cm^2, showing that degradation of OL performance do not originate from NLO properties of the MPA chromophore. It is also important to notice that the OL threshold of the composite is considerably higher than that of the SWNT suspension (approx. 300-400 mJ/cm^2 versus 80 mJ/cm^2). The pi-stacking hypothesis can explain these results : the pi-stacked chromophores can contribute to increase the mass of the absorbing nanoparticles without inducing any increase of absorption cross sections, and they can also play the role of thermal contact resistance, inducing a delay to the formation and growth of scattering centres, leading to increased OL threshold and reduced OL efficiency. Such an effect was shown by pump-probe experiments on carbon black suspensions, the particles being surrounded by surfactant molecules [46].

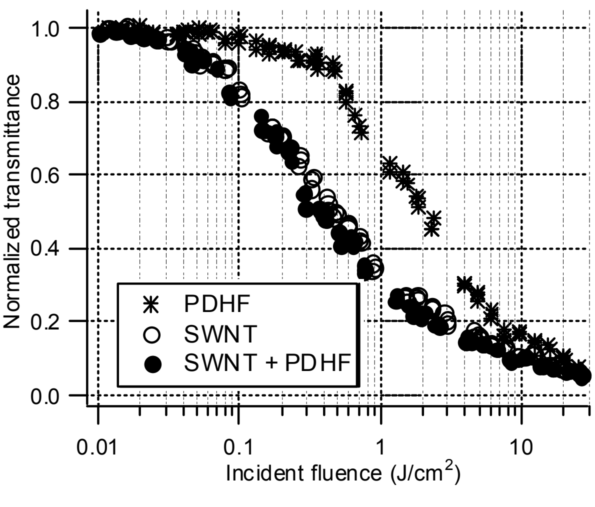


Figure 10 : nonlinear transmittance curves of PDHF, SWNT and composite samples, obtained at 532 nm with 15 ns pulses.

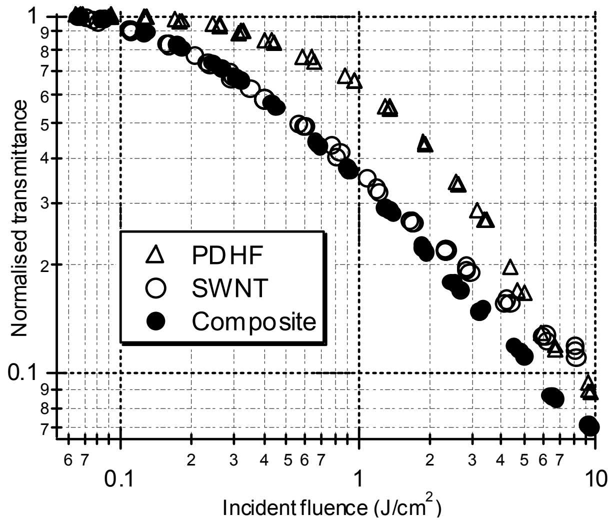


Figure 11 : nonlinear transmittance curves of PDHF, SWNT and composite samples, obtained at 532 nm with 3 ns pulses.

The OL performances of the combined samples seem to be conditioned by the competition between the contribution added by the majority of MPA chromophores which remain in solution, and the adverse (pi-stacking ?) aggregation effect. With 7-ns pulses, the result of that competition is unfavourable to combined samples when compared to SWNT suspensions. But what about other pulse durations? Figures 10 and 11 show results obtained with 15 ns and 3 ns pulses, respectively, on SWNT, PDHF and the combination of both. Limitation of longer pulses should be less sensitive to the retardation of formation and growth of scattering centres, and effectively Fig.10 shows that OL thresholds of SWNT and combined samples are nearly identical, around 20 mJ/cm^2. However, optical limiting efficiency of PDHF is also lower, resulting in OL performance of the SWNT/PDHF nearly identical to that of the SWNT suspension. With 3 ns pulses, better optical response of PDHF allow to counterbalance aggregation effects, resulting in a significant (but not very large) improvement in the performance of SWNT/PDHF sample compared to that of the carbon nanotube suspension.

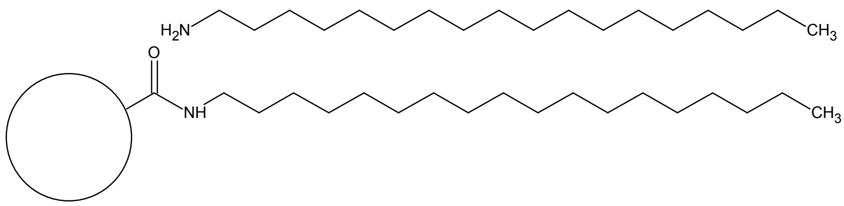
To conclude about the results presented in this section, the benefits expectable from the simple adjunction of multiphoton absorbing chromophores to carbon nanotube suspensions in chloroform are cancelled by an adverse aggregation effect between carbon nanotube bundles and MPA chromophores. Pump-probe experiments are in progress to better understand the influence of that aggregation effect on the response time of nonlinear optical effects. Moreover, this aggregation phenomenon has a dramatic effect on the stability of the samples. The realisation of durable composite samples with enhanced optical limiting performance via cumulative MPA and NLS effects requires solubilisation of carbon nanotubes.

4 . NEW SAMPLES WITH SOLUBILISED CARBON NANOTUBES

4 . 1 Solubilisation of carbon nanotubes

Carbon nanotubes suspensions can be stabilised either by covalent or non-covalent techniques. Non-covalent stabilisation can be achieved using tensio-active species. For example, stable SWNT suspensions in water are obtained by using SDS surfactant. The surfactant moiety consists in an hydrophobic group which stacks at the hydrophobic surface of carbon nanotube bundles, and in a long hydrophilic chain ensuring solubility of the suspended entities, resulting in the avoidance of their aggregation. Carbon nanotube can also be solubilised by embedding in polymer chains, but this relatively thick coating can lead to significant OL performance reduction.

We opted for covalent grafting of long amino-alkyl chains (octadecylamine) onto oxidised carbon nanotubes [37], as shown on Figure 12.



Octadecylamine

Grafting onto carbon nanotube

Figure 12 : functionalisation of carbon nanotubes for their solubilisation in chloroform.

The synthesis was realised at the Commissariat à l'Energie Atomique. Highly purified singlewall carbon nanotube bundles, synthesised by the arc-discharge technique, were purchased from Mer Corporation. Usually, purification techniques involve acidic treatments, inducing some oxidation of carbon nanotubes and resulting in the presence of alcohol and COOH acidic functions at the surface of SWNTs. Further oxidation is forced by acidic reflux, and acid chlorides COCl are obtained from COOH functions by a new reflux with thionyl chloride. The COCl groups are employed as precursors for the covalent bonding of octadecylamine moieties onto carbon nanotubes.

The functionalised carbon nanotubes (designated by **NT-CEA** thereafter) allow to obtain stable solutions, without any aggregation effect. Linear transmittance spectra are nearly identical to those of SWNT suspensions.

4 . 2 Composite samples

The composite samples were elaborated as described in the preceding sections. Their stability was as satisfactory as that of NT-CEA/chloroform samples, the long octadecylamine chains probably preventing pi-stacking of MPA chromophores at the surface of carbon nanotube bundles. Figure 13 shows examples of nonlinear transmittance measurements, performed at 532 nm (3 ns pulses) with solubilised SWNT samples, two different MPA chromophores and the two corresponding NT-CEA/MPA composite samples.

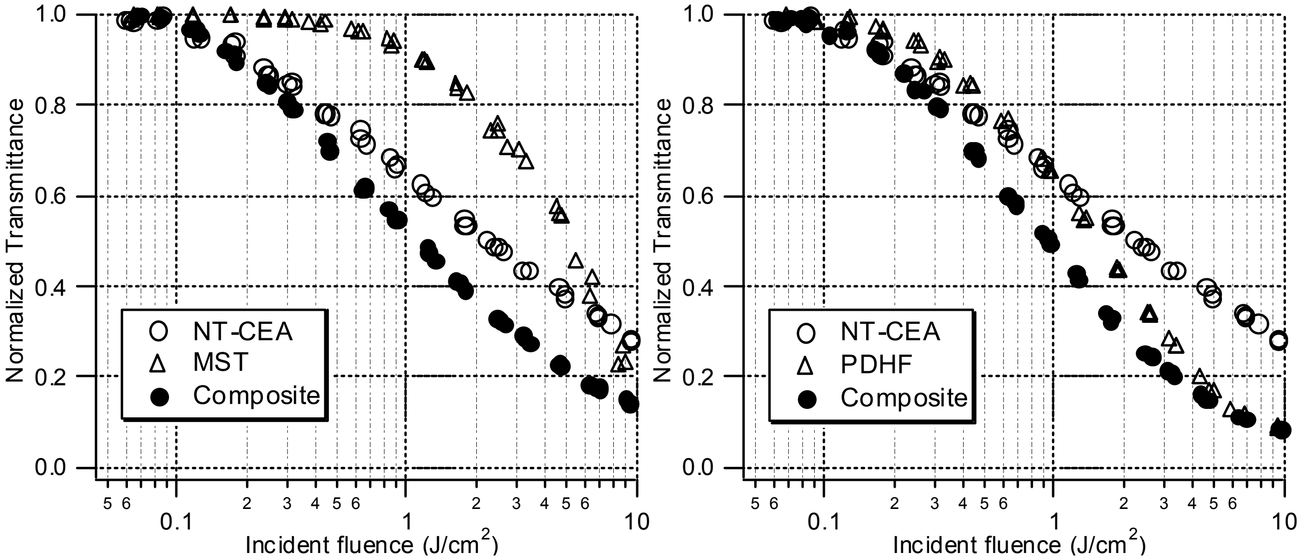


Figure 13 : nonlinear transmittance curves (532 nm, 3 ns pulses) obtained with solubilised nanotube samples, multiphoton absorbing solutions and composite samples. MPA chromophores were modified stilbene-3 (left) and penta-dihexylfluorene (right).

OL performance of NT-CEA samples is poorer than that of the non-functionalised SWNT suspension (cf. Fig.11). It must be related to a three times lower carbon nanotube concentration (linear transmittance of 84 percent at 532 nm for NT-CEA versus 70 percent for SWNT), adopted due to the small available quantity of functionalised carbon nanotubes. The composite samples exhibit significantly reduced nonlinear transmittances, showing the effectiveness of both multiphoton absorption and nonlinear scattering effects.

5 . CONCLUSIONS

A way for the optimisation of optical limiting was proposed, consisting in the combination of nonlinear scattering carbon nanotubes and multiphoton absorbing chromophores at a single intermediate focal plane of sighting systems. The NLO samples consist in suspensions of singlewall carbon nanotubes in multiphoton absorber solutions. Preliminary nonlinear transmittance measurements were performed on composite samples using water as solvent and low concentration of stilbene-3 as MPA chromophores. Encouraging results were obtained, composite samples showing significantly better OL performance than that of simple SWNT/water suspension.

Attempts to optimise OL behaviour were made by using chloroform instead of water as solvent, and by combining carbon nanotubes with highly soluble MPA chromophores possessing higher NLO coefficients. Stability of the composite suspensions was greatly affected by an adverse aggregation effect between carbon nanotubes and chromophores, that effect being also responsible of a significant reduction of optical limiting performance of the composite samples.

Solubilisation of carbon nanotubes in chloroform was realised by covalent grafting of octadecylamine groups, avoiding aggregation effects and allowing the elaboration of new stable composite samples. The OL behaviour of these new materials is promising, with enhanced OL performance due to cumulative nonlinear scattering and multiphoton absorption responses. Further experiments, with increased concentrations of MPA chromophores and of functionalised carbon nanotubes, are needed to fully explore and optimise the new composite materials for optical limiting application.

REFERENCES

1. D. R. Coulter, V. M. Miskowski, J. W. Perry, "Optical limiting in solutions of metallo-phthalocyanines and naphthalocyanines", *SPIE Proceedings,* vol. 1105, 42-51, 1989.
2. J. S. Shirk, R. G. S. Pong, F. J. Bartoli, A. W. Snow, "Optical limiter using a lead phthalocyanine", *Applied Physics Letters* 63 (14), 1880-1882, 1993.
3. C. Li, L. Zhang, M. Yang, H. Wang, Y. Wang, "Dynamic and steady-state behaviors of reverse saturable absorption in metallophthalocyanine", *Physical Review A* 49 (2), 1149-1157, 1994.
4. J. Si, M. Yang, Y. Wang, L. Zhang, C. Li, D. Wang, S. Dong, W. Sun, "Nonlinear absorption in metallo-porphyrin-like", *Optics Communications* 109, 487-491, 1994.
5. K. R. Welford, S. N. R. Swatton, S. Hugues, S. J. Till, G. Spruce, R. C. Hollins, B. S. Wherett, "Nonlinear absorption in organic dyes", *MRS Proceedings*, vol. 374, 239-256, 1994.
6. M. J. Miller, A. G. Mott, G. L. Wood, "Nonlinear behavior of Zn:tetrabenzporphyrin", *SPIE Proceedings*, vol. 2853, 2-11, 1996.
7. A. Sevian, M. Ravikanth, G. R. Kumar, "Optical limiting in short chain basket handle porphyrins", *Chemical Physics Letters* 263, 241-246, 1996.
8. L. W. Tutt, A. Kost, "Optical limiting performances of C_{60} and C_{70} solutions", *Nature* 356, 225-226, 1992.
9. F. Henari, J. Callaghan, H. Stiel, W. Blau, D. J. Cardin, "Intensity-dependent absorption and resonant optical nonlinearity of C_{60} and C_{70} solutions", *Chemical Physics Letters* 199 (1-2), 144-148, 1992.
10. D. McBranch, V. Klimov, L. Smilowitz, M. Grigorova, J. M. Robinson, A. Koskelo, B. R. Mattes, "Femtosecond excited-state absorption dynamics and optical limiting in fullerene solutions, sol-gel glasses, and thin films", *SPIE Proceedings*, vol. 2853, 140-150, 1996.
11. P. D. Fuqua, K. Mansour, D. Alvarez, S. R. Marder, J. W. Perry, B. Dunn, "Synthesis and nonlinear optical properties of sol-gel materials containing phthalocyanines", *SPIE Proceedings,* vol. 1758, 499-506, 1992.
12. F. Bentivegna, M. Canva, P. Georges, A. Brun, F. Chaput, L. Malier, J.-P. Boilot, "Reverse saturable absorption in solid xerogel matrices", *Applied Physics Letters* 62 (15), 1721-1723, 1992.
13. M. Maggini, G. Scorrano, M.Prato, G. Brusatin, P. Innocenzi, M. Guglielmi, A. Renier, R. Signorini, M. Meneghetti, R. Bozio, "C_{60} derivatives embedded in sol-gel silica films", *Advanced Materials* 7 (4), 404-406, 1995.
14. X. D. Sun, X.-J. Wang, W. Shan, J. J. Song, M. G. Fan, E. T. Knobbe, "Nonlinear effects in chromophore doped sol-gel materials", *Journal of Sol-Gel Science and Technology* 9, 169-181, 1997.
15. P. V. Kolinsky, S. R. Hall, M. R. W. Venner, D. F.Croxall, K.Welford, S. Swatton, "Development of solid-state nonlinear absorbers-dyes in polymer hosts", *MRS Proceedings*, vol. 374, 195-199, 1994.
16. S. P. McGeoch, A. Christie, G. S. Bahra, K. R. Welford, "Polymer hosts for non-linear absorbing materials", *MRS Proceedings*, vol. 374, 381-386, 1994.
17. M. Cha, N. S. Sariciftci, A. J. Heeger, J. C. Hummelen, F. Wudl, "Enhanced nonlinear absorption and optical limiting in semiconducting polymer/methanofullerene charge transfer films", *Applied Physics Letters* 67 (26), 3850-3852, 1995.
18. Y. Kojima, T. Matsuoka, H. Takahashi, T. Kurauchi, "Optical limiting property of fullerene-containing polystyrene", *Journal of Materials Science Letters* 16, 2029-2031, 1997.
19. G. S. He, G. C. Xu, P. N. Prasad, B. A. Reinhardt, J. C. Bhatt, A. G. Dillard, "Two-photon absorption and optical-limiting properties of novel organic compounds", *Optics Letters* 20 (5), 435-437, 1995.
20. J. E. Ehrlich, X. L. Wu, L.-Y. S. Lee, A. A. Heikal, Z.-Y. Hu, H. Röckel, S. R. Marder, J. W. Perry, "Two-photon absorbing organic chromophores for optical limiting", *MRS Proceedings*, vol. 479, 9-15, 1997.
21. A. A. Reinhardt, L. L. Brott, S. J. Clarson, R. Kannan, A. G. Dillard, "The design and synthesis of new organic molecules with large two-photon absorption cross-sections for optical limiting applications", *MRS Proceedings*, vol. 479, 3-8, 1997.
22. J. W. Baur, M. D. Alexander, M. Banach, L. R. Denny, B. A. Reinhardt, R. A. Vaia, P. A. Fleitz, S. M. Kirkpatrick, "Molecular environment effects on two-photon-absorbing heterocyclic chromophores", *Chemistry of Materials* 11, 2899-2906, 1999.
23. P.-A. Chollet, V. Dumarcher, J.-M. Nunzi, P. Feneyrou, P. Baldeck, "Dispersion of optical-power limiting in stilbene-3 solutions", *Nonlinear Optics* 21 (1-4), 299-308, 1999.
24. J. W. Perry, S. Barlow, J. E. Ehrlich, A. A. Heikal, Z.-Y. Hu, I.-Y. Lee, K. Mansour, S. R. Marder, H. Röckel, M. Rumi, S. Thayumanavan, X. L. Wu, "Two-photon and higher order absorptions and optical limiting properties of bis-donor substituted conjugated organic chromophores", *Nonlinear Optics* 21, 225-243, 1999.
25. L. Ventelon, S. Charier, L. Moreaux, J. Mertz, M. Blanchard-Desce, "New quadrupolar fluorophores with high two-photon excited fluorescence", *Chemical Communications*, 2055-2056, 1999.
26. Y. Morel, A. Irimia, P. Najechalski, Y. Kervella, O. Stephan, P. L. Baldeck, C. Andraud, "Two-photon absorption and optical limiting of bifluorene molecule", *Journal of Chemical Physics* 114, 5391-5396, 2001.
27. P. Feneyrou, O. Doclot, D. Block, P. L. Baldeck, "Two-photon absorption and optical-limiting properties in dimethylaminocyanobiphenyl crystal", *Journal of Nonlinear Optical Physics and Materials* 5 (4), 767-774, 1996.
28. K. M. Nashold, D. P. Walter, "Temporal and spatial cgaracterization of optical breakdown in a suspension of small absorbing particles", *SPIE Proceedings,* vol. 1105, 78-90, 1989.
29. K. Mansour, M. J. Soileau, E. W. Van Stryland, "Nonlinear optical properties of carbon-black suspensions (ink)", *Journal of the Optical Society of America B* 9 (7), 1100-1109, 1992.

30. A. Fein, Z. Kotler, J. Bar-Sagi, S. Jackel, P. Shaier, B. Zinger, "Nonlinear transmission characteristics of carbon-black suspensions", *Nonlinear Optics* 11, 277-288, 1995.
31. F. Fougeanet, J.-C. Fabre, "Nonlinear mechanisms in carbon-black suspension in a limiting geometry", *MRS Proceedings*, vol. 479, 293-298, 1997.
32. K. J. McEwan, P. K. Milsom, D. B. James, "Nonlinear optical effects in carbon suspensions", *SPIE Proceedings*, vol. 3472, 42-52, 1998.
33. D. Vincent, "High-performance optical limiter based on fine carbon particles suspended in an organic solvent", *Nonlinear Optics* 21 (1-4), 413-422, 1999.
34. X. Sun, Q. Yu, G. Q. Xu, T. S. A. Hor, W. Ji, "Broadband optical limiting with multiwalled carbon nanotubes", *Applied Physics Letters* 73 (25), 3632-3634, 1998.
35. L. Vivien, E. Anglaret, D. Riehl, F. Bacou, C. Journet, C. Goze, M. Andrieux, M. Brunet, F. Lafonta, P. Bernier, F. Hache, "Singlewall carbon nanotubes for optical limiting", *Chemical Physics Letters* 307, 317-319, 1999.
36. S. R. Mishra, H. S. Rawat, S. C. Mehendale, K. C. Rustagi, A. K. Sood, R. Bandyopadhyay, C. N. R. Rao, "Optical limiting in single-walled carbon nanotubes", *Chemical Physics Letters* 317, 510-514, 2000.
37. J. E. Riggs, D. B. Walker, D. L. Caroll, Y.-P. Sun, "Optical limiting properties of suspended and solubilized carbon nanotubes", *Journal of Physical Chemistry B* 104 (30), 7071-7076, 2000.
38. A. A. Said, T. H. Wei, R. De Salvo, Z. Wang, M. Sheik Bahae, D. J. Hagan, E. W. Van Stryland, "Self-protecting optical limiters using cascading geometries", *SPIE Proceedings*, vol. 1692, 37-43, 1992.
39. P. A. Miles, "Bottleneck optical limiters: the optimal use of excited-state absorbers", *Applied Optics* 33 (30), 6965-6979, 1994.
40. A. A. Said, T. Xia, D. J. Hagan, A. Wajsgrus, S. Yang, D. Kovsh, M. A. Decker, S. Khodja, E. W. Van Stryland, "Liquid-based multicell optical limiter", *SPIE Proceedings*, vol. 2853, 158-169, 1996.
41. P. Feneyrou, "Broadband optical limiting using tandem filters with multiphoton absorber and reverse saturable absorbers", *Journal of Nonlinear Optical Physics and Materials* 9 (4), 523-530, 2000.
42. M. Meneghetti, R. Signorini, R. Bozio, M. Maggini, G. Scorrano, M. Prato, G. Brusatin, M. Guglielmi, "Optical limiting of multilayer sol-gel structures containing fullerenes", *Synthetic Metals* 103, 2474-2475, 1999.
43. R. Signorini, D. Pedron, C. Ferrante, R. Bozio, G. Brusatin, P. Innocenzi, F. Della Negra, M. Maggini, S. Abotto, L. Beverina, G. Pagani, "Optical limiting based on multiphoton processes in carbon nanostructures and heterocyclic quadrupolar molecules", *SPIE Proceedings*, vol. 4797, 1-14, 2002.
44. E. W. Van Stryland, S. S. Yang, F. E. Hernandez, V. Dubikovsky, W. Shensky, D. J. Hagan, "Cascaded optical limiters and modelling", *Nonlinear Optics* 27 (1-4), 181-192, 2001.
45. K. J. McEwan, P. A. Madden, "Transient grating effects in absorbing colloidal suspensions", *Journal of Chemical Physics* 97 (11), 8748-8759, 1992.
46. F. Fougeanet, D. Riehl, "Investigation of optical limiting mechanisms in carbon-black suspensions", *Nonlinear* Optics 21 (1-4), 435-446, 1998.
47. R. Goedert, R. Becker, A. Clements, T. Whittaker, "Time-resolved shadowgraphic imaging of nonlinear liquids and suspensions", *SPIE Proceedings*, vol. 2853, 54-72, 1996.
48. L. Vivien, D. Riehl, P. Lançon, F. Hache, E. Anglaret, "Bubble growth and cavitation in carbon nanotube suspensions", *Nonlinear Optics* 27, 395-403, 2001.
49. L. Vivien, D. Riehl, J.-F. Delouis, J. A. Delaire, F. Hache, E. Anglaret, "Picosecond and nanosecond polychromatic pump-probe studies of bubble growth in carbon-nanotube suspensions", *Journal of the Optical Society America B* 19 (2), 208-214, 2002.
50. L. Vivien, J. Moreau, D. Riehl, P.-A. Alloncle, M. Autric, F. Hache, E. Anglaret, "Shadowgraphic imaging of carbon nanotube suspensions in water and in chloroform", *Journal of the Optical Society America B* 19 (11), 2665-2672, 2002.
51. O. Mongin, L. Porrès, L. Moreaux, J. Mertz, M. Blanchard-Desce, "Synthesis and photophysical properties of new conjugated fluorophores designed for two-photon-excited fluorescence", *Organic Letters* 4, 719-722, 2002.
52. L. Ventelon, L. Porrès, M. Blanchard-Desce, Y. Morel, P. Baldeck, P. Feneyrou, M. Silly, P.-A. Chollet, "Biphenyl derivatives with enhanced nonlinear absorptivities for optical limiting applications", *SPIE Proceedings*, vol. 4797, 15-24, 2002.
53. R. Anémian, J.-C. Mulatier, C. Andraud, Y. Morel, O. Stephan, P. L. Baldeck, "Two-photon induced nonlinear absorption in fluorene oligomers", *SPIE Proceedings*, vol. 4797, 25-32, 2002.