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Organic and inorganic optical limiting materials. From fullerenes to nanoparticles

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Optical limiting properties of organic reverse saturable absorbers, fullerenes, and nanoscopic materials are reviewed. The strongly nonlinear absorptive organic dyes are discussed in terms of the potential and limitation in their further improvement. The principle and practice for the development of supramolecular nonlinear absorbers based on a new molecular engineering approach are described along with future prospects. The fullerene based materials are discussed by emphasizing the mechanistic issues of their optical limiting properties and the potential for improving their optical limiting performance through fullerene cage derivatizations and through the incorporation of fullerene cages into polymeric structures. Finally, the discussion on the development of nano-materials as a new class of strong optical limiters is centred on the optical limiting performance and mechanism of metal and metal sulphide nanoparticles, and on a comparison with strongly nonlinear scattering materials such as suspensions of carbon black particles. The review also includes a comprehensive list of references on optical limiting materials.

1. Introduction

The development of modern optical technology demands the ability to control the intensity of light in a predetermined and predictable manner. For the manipulation of optical beams in the passive method [1], nonlinear optical materials whose transmittance decreases significantly with increasing light fluence have received much recent attention [1–3]. These materials and related devices are called optical limiters or optical power limiters. There is great current interest in the development of organic and inorganic optical limiting materials for applications ranging from the protection of optical sensors from laser irradiation to all-optical switching. Some of these applications are discussed in recent symposium proceedings [4–6].

An ideal optical limiter exhibits linear transmission below a fluence threshold, but above this threshold the transmission becomes highly nonlinear, with the output light intensity reaching a plateau (figure 1). The development of potent optical limiters has proven to be a rather challenging task because strong optical limiting materials are scarce. While many strategies have been employed for attenuating light intensity, the use of nonlinear optical materials that exhibit either strong nonlinear absorptive or strong nonlinear scattering responses is apparently the most promising in the limiting of nanosecond or picosecond laser pulses. Recently, however, materials of large two-photon absorption cross-sections have attracted much attention [7–14]. Among potent nonlinear absorptive materials under active investigations are organic dyes such as metalloporphyrins and metallophthalocyanines [2, 15–32], mixed metal complexes and clusters [33–41], and fullerenes [42–86]. Strongly optical limiting nanoscopic materials may also be included in the same category [87, 88]. Considering the fact that there have been several recent reviews on the history and current

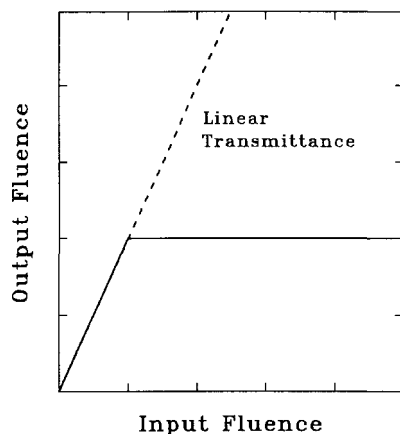


Figure 1. Nonlinear response of an ideal optical limiter.

activities in the development of optical limiting materials and devices [1–3], here we provide a review on materials of strong optical limiting responses from a somewhat different angle. The strongly nonlinear absorptive organic dyes are discussed in terms of the potential and limitation in their further improvement. The principle and practice for the development of supramolecular nonlinear absorbers based on a new molecular engineering approach are provided along with future prospects. The fullerene based materials are discussed by emphasizing the mechanistic issues of their optical limiting properties and the potential for improving their optical limiting performance through fullerene cage derivatization and through the incorporation of fullerene cages into polymeric structures. Finally, the discussion on the development of nano-materials as a new class of strong optical limiters is centred on the optical limiting performance and mechanism of metal and metal sulphide nanoparticles, and on a comparison with strongly nonlinear scattering materials such as suspensions of carbon black particles. The review also includes a comprehensive list of references available in the literature on optical limiting materials.

2. Nonlinear absorptive organic dyes

Nonlinear absorptive organic dyes are among the most widely studied optical limiting materials [2, 15–32, 89–96]. The nonlinear absorption in the dyes is due to photoinduced formation of an absorbing state whose absorption cross-section is higher than that of the ground state at the excitation wavelength. The phenomenon is commonly referred to as reverse saturable absorption, and the materials with such a property are often called reverse saturable absorbers. Not surprisingly, typical reverse saturable absorbers have weak ground state absorptions at the concerned wavelengths. It is also not a coincidence that most of the organic nonlinear absorbers under active investigation are symmetric molecules, whose low-lying electronic transitions are only weakly allowed.

The most common mechanism for organic reverse saturable absorbers is the formation of strongly absorptive excited singlet and/or triplet state(s). Since the nonlinear absorptive organic dyes under consideration for optical limiting are typically large polyatomic molecules, vibrational relaxation in the electronic excited states is very fast, likely on the time scale of a few picoseconds or even sub-picosecond. As a

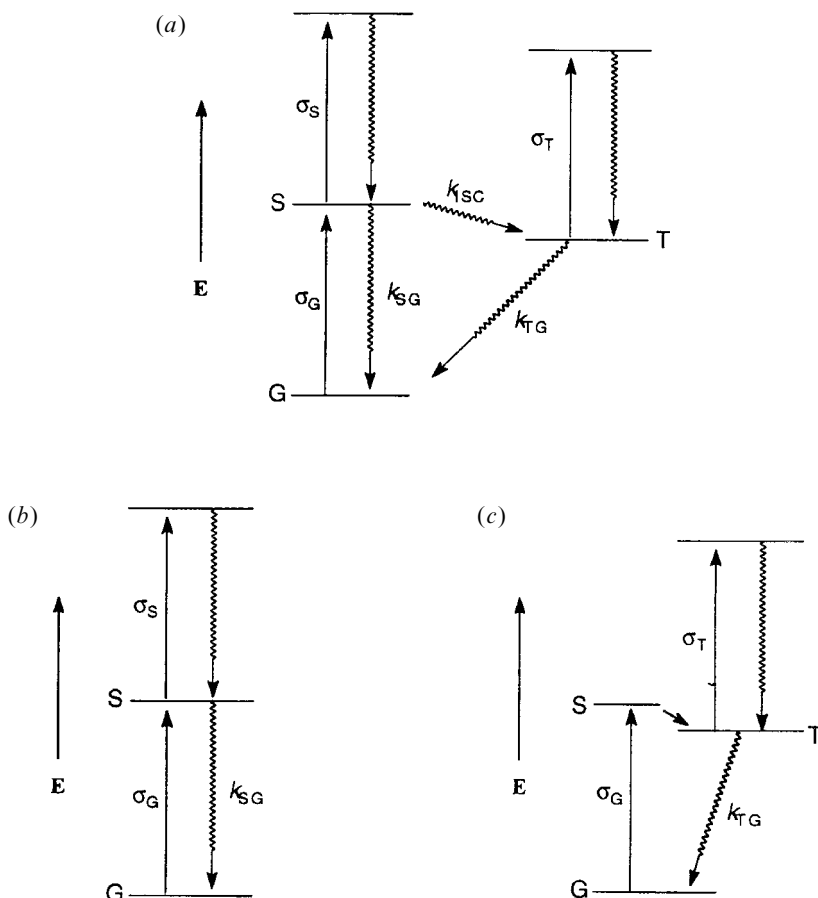


Figure 2. (a) The five level reverse saturable absorption model. (b) A simplified model for reverse saturable absorption dominated by the excited singlet state absorption. (c) A simplified model for reverse saturable absorption dominated by the excited triplet state absorption.

result, even for the limiting of picosecond laser pulses, only the vibrationally relaxed lowest electronic excited states need to be considered in a mechanistic description of reverse saturable absorption. Figure 2(a) shows a five-level scheme commonly used for organic reverse saturable absorbers. The fundamental differential equation for the five-level scheme is written as follows.

$$di/dx = -i(\sigma_G N_G + \sigma_S N_S + \sigma_T N_T), \quad (1)$$

where i represents the photon flux (photons $\text{cm}^{-2} \text{s}^{-1}$) changes with distance x through the sample of a path length L , σ denotes absorption cross-sections (cm^2) of the electronic states shown in figure 2(a), and N represents the molecular populations in the different states. Under the assumption of negligible populations in the upper excited states, the changes in the state populations with time are typically described as follows.

$$dN_S/dt = \sigma_G N_G i - (k_{SG} + k_{ISC}) N_S, \quad (2)$$

Table 1. Selected strong reverse saturable absorbers for optical limiting at 532 nm.

Molecule	τ_f (ns)	Φ_{ISC}	σ_S/σ_G	σ_T/σ_G	σ_{EFF}/σ_G	Reference
InClPc(<i>t</i> -butyl) ₄	0.3	0.88			30±6	[2, 15]
AlClPc	7.0	0.35	10	20	12	[2, 16, 17]
PbPc	0.35	0.92	30	23	24	[2, 19–22]
CdCl texaphyrin	0.1	0.9	7.7		2.4	[2, 31 (g)]
H ₂ <i>meso</i> -tetraphenylporphyrin	9.0		3.8			[2, 28, 106]
Zn <i>meso</i> -tetraphenylporphyrin	1.5		2.6			[2, 28, 106]
Co <i>meso</i> -tetraphenylporphyrin	< 0.1				3.0	[2, 28, 106]
Zn <i>meso</i> -tetraphenyltetrabenzoporphyrin	0.65		4.2			[2, 30]
King's complex (Fe(CO)Cp) ₄	0.12		~ 2			[2, 34–36]
Polymethine dye	0.3		80			[96]
(<i>n</i> -Bu ₄ N) ₃ [MoA ₃ BrX ₃ S ₄]					6–8	[2, 38, 39]
Indanthrone					3	[2, 90]
[60]Fullerene	1.2	1.0			3.1 ± 0.3	[15, 61, 155]

$$dN_T/dt = k_{ISC}N_S - k_{TG}N_T. \quad (3)$$

An expression for N_G is not necessary because of the relationship $N_G = N_0 - (N_S + N_T)$, where N_0 is the total molecular population. For short laser pulses on the picosecond time scale, the condition for reverse saturable absorption is effectively that the excited singlet state absorption cross-section is larger than the ground state cross-section, $\sigma_S/\sigma_G > 1$, because the excited triplet state population is often negligible in the laser pulse duration. Under such a condition, the five-level scheme shown in figure 2 (a) is effectively reduced to a three-level scheme shown in figure 2 (b).

The reverse saturable absorption for limiting laser pulses of a few nanoseconds or longer may be evaluated by the required absorption cross-section ratio $\sigma_{EFF}/\sigma_G > 1$, where σ_{EFF} is a weighted average of σ_S and σ_T [15]. The weight factor for σ_{EFF} depends on the excited triplet state rise time and the intersystem crossing yield of the molecule under consideration. In the limit that the excited triplet state rise time is shorter than the laser pulse duration, the ratio σ_{EFF}/σ_G for reverse saturable absorption may be simplified to $\Phi_{ISC}\sigma_T/\sigma_G$, where Φ_{ISC} is the intersystem crossing yield. Again, the five-level scheme shown in figure 2 (a) is effectively reduced to a three-level scheme shown in figure 2 (c). Nevertheless, many reverse saturable absorptive organic dyes limit nanosecond laser pulses by contributions from both the excited singlet and triplet state absorptions. Summarized in table 1 are commonly used organic dyes of optical limiting responses toward nanosecond and/or picosecond laser pulses.

In a recent review [3], Perry compared the optical limiting properties of different classes of organic and metal-containing reverse saturable absorbers. Among the materials of the best optical limiting performance toward the second harmonic of a Q-switched Nd:YAG laser at 532 nm are metallophthalocyanines (metallo-Pcs), especially with indium (**1**, see scheme 1) or lead (**2**, see scheme 1) as the centre metal [15, 19, 21–23]. The metallo-Pcs all have strong absorptions in the excited singlet and triplet states. However, what makes the molecules so special is really their extremely weak ground state absorption at the laser wavelength. As shown in figure 3, there is a deep valley in the absorption spectrum of chloroaluminium phthalocyanine in a narrow wavelength region around 532 nm. With the extremely small ground state absorption cross-sections of the metallo-Pcs, σ_G of $2.2 \times 10^{-18} \text{ cm}^2$

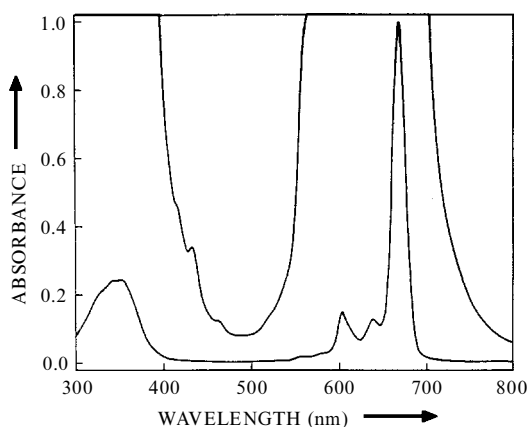
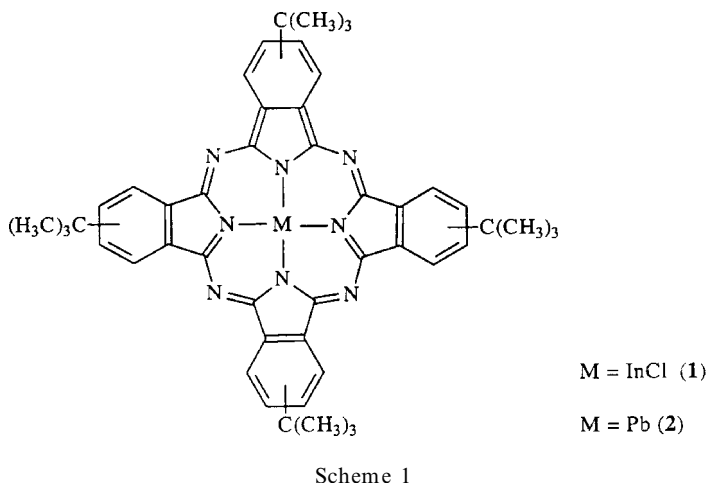


Figure 3. Absorption spectra of AlClPc in ethanol solutions of $\sim 4 \times 10^{-6}$ M (lower trace) and 3.2×10^{-4} M (upper trace). (From [17]: with kind permission from Kluwer Academic Publishers.)

or molar absorptivity of $580 \text{ M}^{-1} \text{ cm}^{-1}$ [18] for AlClPc, the $\sigma_{\text{EFF}}/\sigma_{\text{G}}$ ratios are large for reverse saturable absorption. The $\sigma_{\text{EFF}}/\sigma_{\text{G}}$ ratios are particularly large in InClPc and PbPc due to their higher intersystem crossing yields, which are attributed to heavy atom effects [15, 22, 23]. Shown in figure 4 is a comparison of the optical limiting results of InClPc and other materials at 532 nm. Because of the ground state absorption pattern, the metallo-Pcs are narrow-band optical limiting materials, effective only in a narrow wavelength range. For practical applications, however, the strong ground state absorptions in the rest of the visible wavelength region (figure 3) provides the effect of a band-pass filter, linearly limiting the light transmission.

The development of stronger reverse saturable absorbers and new optical limiting materials in general has been progressing rather slowly. The slow progress is understandable because of the tough requirement for a material to be strongly nonlinear absorptive. The potential for significantly improving the performance of existing reverse saturable absorbers through chemical modification seems limited.

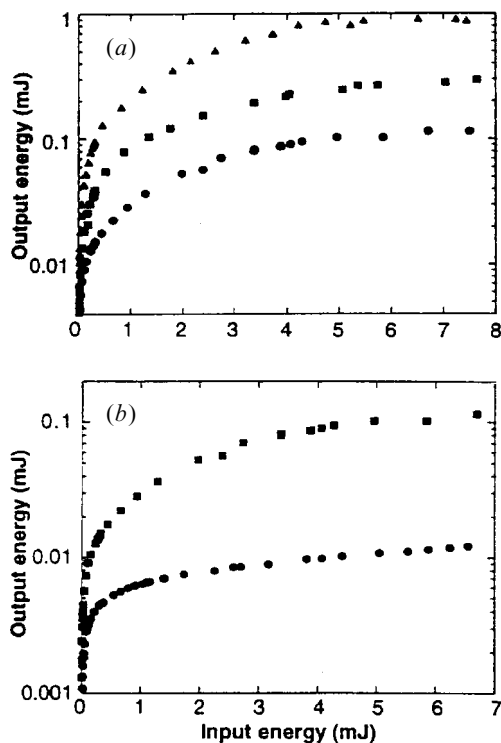


Figure 4. From [15] with the original caption: (a) optical limiting response of C_{60} in toluene (\blacktriangle), AlClPc in methanol (\blacksquare) and InClPc(t-butyl) $_4$ in toluene (\bullet) in an $f/5$ optical system as measured with 8 ns, 532 nm laser pulses. All the solutions had a linear transmittance of 70% in a cell with pathlength of 1 cm. (b) Optical limiting response of a homogeneous solution of InClPc(t-butyl) $_4$ in toluene (\blacksquare) and a three disc InClPc(t-butyl) $_4$ -PMMA optical limiter (\bullet). The concentration of InClPc(t-butyl) $_4$ discs (total thickness of 2.1 mm) was $\sim 1.5 \times 10^{-3}$ M, resulting in an internal transmittance of 70% for the set of discs. Other experimental details are as for (a). Reprinted with permission from Perry *et al.*, *Science*, **273**, 1533. Copyright 1996 American Association for the Advancement of Science. Readers may view, browse, and/or download this material for temporary copying purposes only, provided these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published, or sold in whole or in part, without prior written permission from AAAS.

For limiting nanosecond laser pulses, the performance of nonlinear absorptive organic dyes is determined by the effective cross-section ratio, $\sigma_{\text{EFF}}/\sigma_{\text{G}}$. The ground state absorption cross-section σ_{G} is necessarily small in reverse saturable absorbers, which are typically associated with molecules of nearly forbidden or weakly allowed electronic transitions. In fact, the most promising nonlinear absorptive organic dyes under active investigation are all highly symmetric molecules, in which electronic transitions to the low-lying excited states are only weakly allowed. While it is certainly practical to affect the electronic transition probabilities through molecular structural modifications such as derivatizations, the changes thus obtained are in the wrong direction with respect to increasing nonlinear absorptive responses. A reduction in molecular symmetry as a result of derivatization most likely enhances

ground state electronic transition probabilities, corresponding to a larger absorption cross-section σ_G and a smaller σ_{EFF}/σ_G ratio.

The general relationships between molecular structure and excited state absorption cross-sections are not well established. A lack of such relationships presents a difficult task in the effort of improving the nonlinear absorptive responses of existing materials through molecular structural modifications. The available experimental triplet-triplet absorption results of organic molecules seem to suggest that excited state absorption cross-sections of different derivatives in a compound class do not vary in a dramatic fashion [97, 98]. Thus, the potential for improving nonlinear absorptive responses through appropriate functionalizations of existing optical limiting organic dyes is probably limited as well. In fact, the successful examples of obtaining larger excited state absorption cross-section σ_{EFF} by structurally modifying the existing nonlinear absorptive organic dyes are associated with the enhancement of intersystem crossing efficiencies in the dye molecules [15, 23]. For metallo-Pcs, intersystem crossing yields of the molecules with a heavy metal in the centre are significantly higher. For example, the intersystem crossing yield increases from 0.35 in AlClPc to 0.88 in InClPc, resulting in a corresponding increase in the effective excited state absorption cross-section σ_{EFF} [2]. However, the potential for further improvement in the optical limiting performance of metallo-Pcs in such a mechanism is obviously limited because the intersystem crossing yield can only be increased to the absolute maximum of unity.

Discoveries of new nonlinear absorptive organic dyes have been scarce. The conclusion by Van Stryland *et al.* [3] is well justified that very little progress has been made at developing strong optical limiters in thin film form to limit nanosecond and shorter pulses. The recent discoveries of new nonlinear absorptive optical limiting materials include mixed metal clusters [38–40] and fullerenes [42]. According to Shi *et al.*, the mixed metal clusters have better optical limiting performance than [60]fullerene (C_{60}), a benchmark material [38]. However, the C_{60} optical limiting results used in the comparison are very different from those reported by Tutt and Kost [38, 42]. In fact, if the latter was used in the comparison the optical limiting performance of C_{60} in toluene solution would have been better [38, 42]. In a separate note, there is a recent suggestion that optical limiting responses of the mixed metal clusters may be explained in terms of the same nonlinear scattering mechanism for carbon black suspensions [41]. The optical limiting performance of C_{60} and C_{70} also falls short of that of metallo-Pcs at 532 nm (figure 4) [15].

The difficulty with the availability of superior reverse saturable absorbers for optical limiting is due to the tough requirement imposed on such materials. For limiting nanosecond laser pulses, a single molecular species is required to possess three important properties for reverse saturable absorption, namely weak ground state absorption, strong excited state absorption, and a very high intersystem crossing yield [15, 23]. There are just not many organic dyes that have all of these properties. From the materials development point of view, the *development* of superior nonlinear absorptive materials should be dependent on the design and synthesis of new materials from available precursors of known ground and excited state properties, rather than dependent on the accidental emergence of a new class of materials. In other words, the further advance and breakthrough in the development of potent reverse saturable absorbers will most likely come from a molecular engineering approach. There are in fact plenty of organic molecules that have one or two of the three properties required for strong nonlinear absorption. These molecular species may be used as building

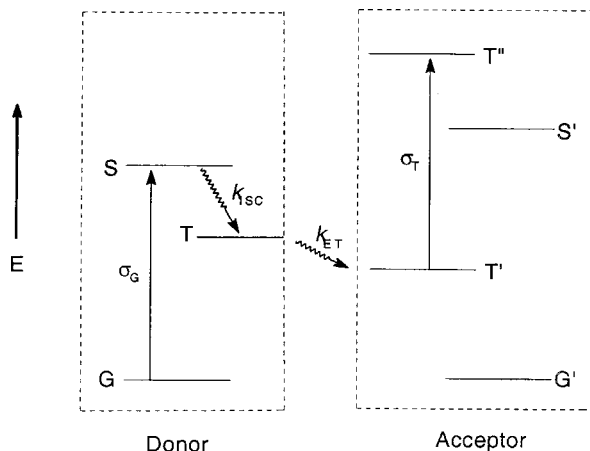
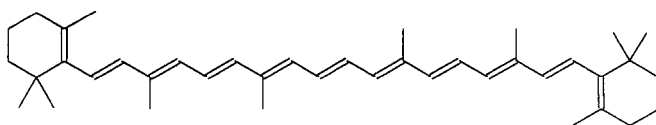


Figure 5. The energy level diagram for an ideal SupraRSA optical limiter based on triplet energy transfer [99].

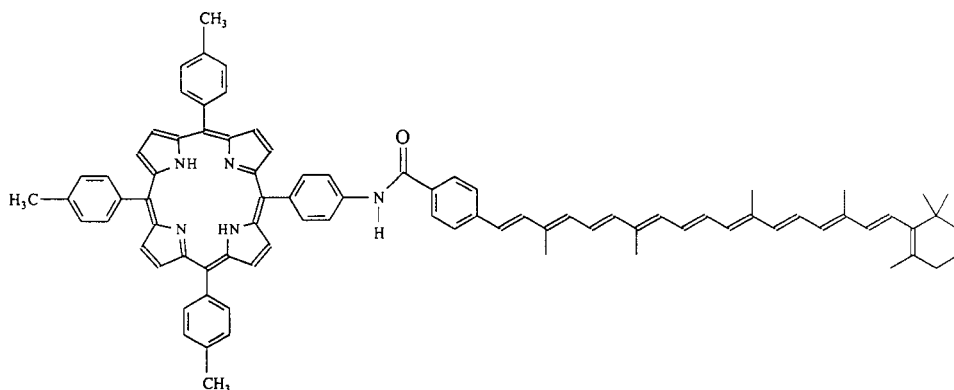
blocks in molecular engineering. Sun and co-workers recently proposed a new concept based on molecular engineering for the design and synthetic preparation of supramolecular reverse saturable absorbers (SupraRSA) for strong optical limiting at concerned wavelengths or in a concerned wavelength range [99]. Since the molecular building blocks for SupraRSAs are only required to possess one or two of the three properties discussed above for strongly nonlinear absorptive organic dyes and therefore readily available, the new molecular engineering strategy offers the opportunity for developing reverse saturable absorbers of much better optical limiting performance than the existing single molecular species nonlinear absorptive organic dyes.

Electronic energy donor–acceptor dyads represent simple examples of the SupraRSAs [99]. In a supramolecular donor–acceptor dyad, two sub-structures of the supramolecule are each responsible for the required weak ground state absorption and extremely strong excited state absorption at the laser wavelength. Shown in figure 5 is the energy diagram for an ideal triplet energy donor–acceptor dyad for nonlinear absorptive optical limiting [99]. The requirements for the donor and acceptor are weak ground state absorption and strong excited triplet state absorption, respectively. For the donor and acceptor as a pair, it is also required that the electronic energy transfer is so fast that the rise time of the strongly absorptive acceptor excited triplet state is shorter than the laser pulse width.

In principle, electronic energy donor–acceptor pairs could be either intramolecular or intermolecular. For example, Sun and co-workers examined an intermolecular donor–acceptor pair in which C_{60} was the triplet energy donor and β -carotene (β -CT) (scheme 2) was the triplet energy acceptor in a room-temperature toluene solution [99]. With an intersystem crossing yield of unity, C_{60} is a perfect triplet photosensitizer [100, 101] to populate the excited triplet state of β -CT quantitatively. The triplet–triplet absorption of β -CT peaks at 530 ~ 540 nm [102] with an extremely large molar absorptivity $\epsilon_{T,MAX}$ of $\sim 200\,000\text{ M}^{-1}\text{ cm}^{-1}$ (cross-section $\sigma_{T,MAX}$ of $\sim 7.64 \times 10^{-16}\text{ cm}^2$) [97, 98]. Despite the extremely large σ_T and relatively weak ground state absorption at 532 nm, β -CT itself is not a strong nonlinear absorber for optical limiting [103] because of its negligible intersystem crossing yield [97, 98]. In the C_{60} – β -CT pair, the combined absorption cross-section ratio between acceptor



Scheme 2.



Scheme 3.

and donor, $\sigma_{T,A}/\sigma_{G,D}$, is 200 or higher at 532 nm, representing the great potential for extremely strong nonlinear absorptive optical limiting. However, in order to use the donor–acceptor pair in the limiting of nanosecond laser pulses, the triplet energy transfer has to be very fast, which requires an extremely high β -CT concentration [99]. In terms of the Stern–Volmer quenching equation, the requirement is such that the triplet state lifetime of the donor C_{60} in the presence of β -CT ($1/k_q[\beta\text{-CT}]$) should be shorter than the laser pulse width. Thus, even with the quenching rate constant k_q being diffusion-controlled, a β -CT concentration of 0.1 M or higher is necessary. A significant problem with such a required high acceptor concentration is the limited solubility of β -CT in room-temperature solution. More importantly, at such a high β -CT concentration, the very weak but meaningful ground state absorption of β -CT at 532 nm becomes competitive to the weak ground state absorption of the donor C_{60} [99]. As a result, the donor–acceptor pair no longer satisfies the requirements for SupraRSAs as discussed above with the energy diagram shown in figure 5. It is therefore understandable that hardly any optical limiting responses were observed for the intermolecular C_{60} – β -CT pair in room-temperature toluene solution toward nanosecond laser pulses at 532 nm [99]. The problems encountered in the C_{60} – β -CT system are typical with respect to intermolecular donor–acceptor pairs because the rapid energy transfer requires the efficient quenching of the donor excited triplet state by an extremely high concentration of acceptor molecules. It was thus concluded [99] that practical applications of the SupraRSA concept most likely require the use of intramolecular donor–acceptor dyads. An additional advantage of intramolecular SupraRSAs is that the optical limiting materials thus obtained may be used with solid-state matrices in practical optical devices because no diffusional quenching is required in the energy transfer. However, a significant disadvantage with intramolecular donor–acceptor dyad optical limiters is that synthetic preparations of the supramolecules are always very challenging.

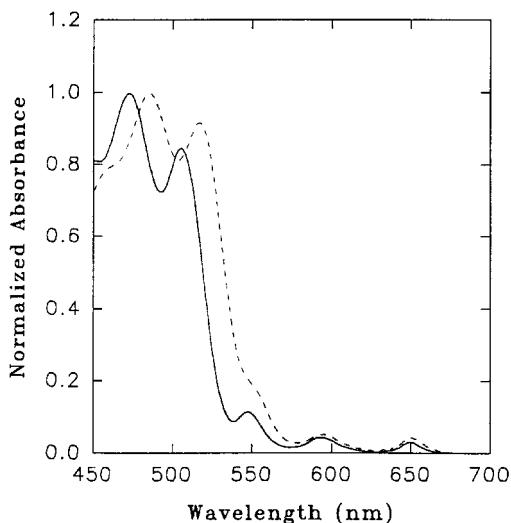


Figure 6. Absorption spectra of the carotenoporphyrin dyad **4** in room-temperature toluene (dashed line) and hexane (solid line) [104].

Sun *et al.* [104] have examined optical limiting properties of the dyad carotenoporphyrin **4** (scheme 3) as a candidate for SupraRSA. It is known that upon photoexcitation the dyad **4** undergoes efficient intramolecular triplet energy transfer [105]. Figure 6 shows the ground state absorption spectra of the dyad **4** in room-temperature toluene and hexane. The ground state absorption in toluene at 532 nm is dominated by the carotene moiety. As a result, there is essentially no nonlinear absorptive optical limiting for the dyad **4** in room-temperature toluene solution (figure 7) [104]. Since the ground state absorption of the carotene moiety blue-shifts with decreasing solvent refractive index and the absorption of the porphyrin moiety is relatively inert to solvent changes, the ground state absorption of the supramolecule in hexane at 532 nm consists of a significant contribution from the porphyrin moiety (figure 6). As a result, significant optical limiting toward 5 ns laser pulses at 532 nm was observed for the carotenoporphyrin dyad **4** in room-temperature hexane solution (figure 7) [104]. However, whether the observed optical limiting responses are due to the nonlinear absorption of the porphyrin moiety alone or due also to the strong absorption of the carotene excited triplet state [105], which is populated through intramolecular triplet energy transfer, remains to be evaluated and determined. A problem with the free-base porphyrin as a triplet energy donor is that the triplet state rising is slow (9 ns [106]) for limiting 5 ns laser pulses. A metalloporphyrin such as zinc porphyrin of fast triplet state rising time (1.5 ns [106]) should have a better triplet energy donor moiety in the supramolecular dyad for optical limiting on the nanosecond time scale [104].

The design, preparation, and evaluation of SupraRSAs represent a new strategy in the development of stronger nonlinear absorptive optical limiters based on molecular engineering [99, 104]. In the supramolecules, the nonlinear absorption is achieved by a combination of two molecular species, namely that strong reverse saturable absorbers are built from molecules which themselves may show no nonlinear absorptive responses at all. Since the new strategy is subject to much less restrictions than the traditional approach based on the discovery of new material classes, it offers essentially unlimited possibilities in the development of potent optical limiting materials.

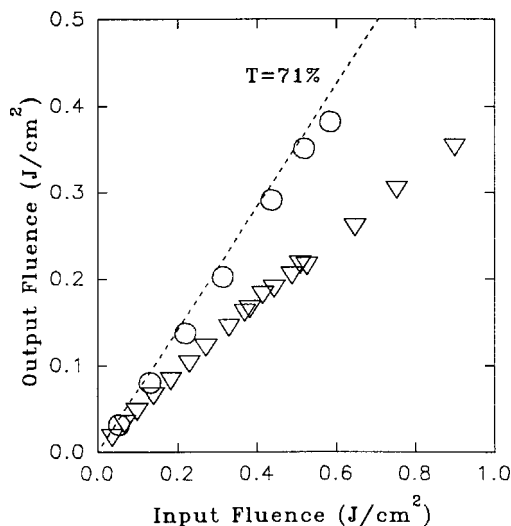


Figure 7. Optical limiting results (5 ns laser pulses) of the carotenoporphyryn dyad **4** in room-temperature toluene (○) and hexane (▽) solutions of 71% linear transmittance at 532 nm [104].

SupraRSAs do not necessarily need a triplet energy transfer mechanism. In fact, redox dyads in which the two sub-units are electron donor and acceptor offer more flexibility. Figure 8 shows the energy diagram for an ideal redox dyad SupraRSA. Because the molecular ground state absorption is typically in a different wavelength region from the molecular ion absorption, there should be less interference from the ground state absorption of the sub-unit that is responsible for strong transient absorption. Thus, it may even be possible to achieve strong nonlinear absorptive optical limiting in solution by use of an intermolecular redox pair. The recent work by Perry and co-workers [107] may be classified into this category. It was shown [107] that photoinduced intermolecular charge transfers are responsible for optical limiting in solutions that contain photosensitizers and electron acceptors. Tricarbocyanine dyes were used as photosensitizers, and porphyrins and several viologen derivatives were used as electron acceptors. Strongly absorptive charge separated species generated from the photosensitization are likely responsible for the observed optical limiting responses [107]. Prasad and co-workers have also used intense illumination to generate cationic and dicationic states of an electron donor using C_{60} as an electron acceptor [108]. The cationic and dicationic states are highly absorptive transients, resulting in strong reverse saturable absorption. Finally, the optical limiting results of fullerenes in aromatic amine solvents [109] may also be understood in terms of the nonlinear absorption that is associated with photoinduced redox processes (see below).

Nonlinear absorptive organic dyes are commonly used as model compounds in the design of optimized optical limiting devices for a focused beam geometry [110–116]. Because the device design and optimization rely heavily on the accuracy of absorptivity and excited state parameters, the photophysical properties of the widely used model reverse saturable absorbers may need to be re-evaluated and determined in a more quantitative fashion.

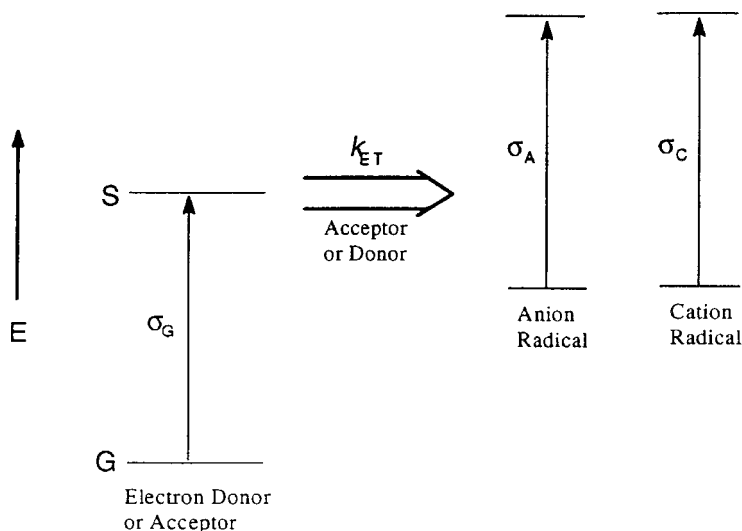


Figure 8. The energy level diagram for an ideal SupraRSA optical limiter based on photo-induced electron transfer and strong absorptions of the charge separated species.

3. Fullerenes

Fullerenes are structurally defined symmetric all carbon clusters. The discovery of optical limiting properties in fullerene materials represents one of the most significant recent developments in the search for new optical limiters.

Tutt and Kost first reported [42] that C_{60} in toluene solution is an excellent optical limiter toward a nanosecond pulsed Nd:YAG laser at 532 nm. It was shown that C_{60} has better optical limiting performance than most of the known optical limiting materials at the time [42]. Since the discovery, there have been extensive investigations of fullerene optical limiting properties [43–86, 117–120]. The investigations may be classified in terms of three categories: (1) the optical limiting properties of fullerenes in different media and under different conditions, (2) effects of fullerene cage functionalizations on the optical limiting properties, and (3) mechanistic details on the optical limiting properties of fullerenes and related materials. In addition to C_{60} , other members of the fullerene family, including C_{70} , C_{76} , C_{78} , and C_{84} in room-temperature solutions, have been investigated for their optical limiting responses toward nanosecond laser pulses [117, 118]. The results show that C_{60} is by far the best in the fullerene family for optical limiting performance at 532 nm.

3.1. Optical limiting under different conditions

The optical limiting responses of C_{60} at different wavelengths and in different solvents have been reported. The results obtained at different wavelengths are very different, with the best performance in the far red wavelength region. The wavelength dependence was considered as evidence in support of a reverse saturable absorption mechanism for the optical limiting properties of fullerenes (see below). While it is generally true that the optical limiting responses of C_{60} in solution are insensitive to solvent changes [59 (b), 80, 81] the same conclusion cannot be applied to the results in solvents of electron donating characteristics [46, 109]. For C_{60} in *N,N*-diethylaniline (DEA) or *N,N*-dimethylaniline (DMA) solution for example, the optical limiting

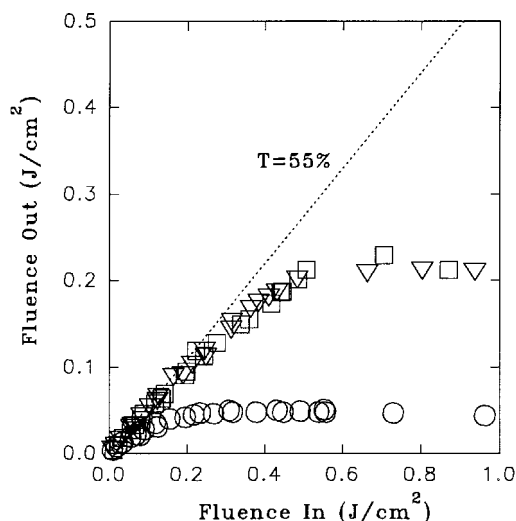
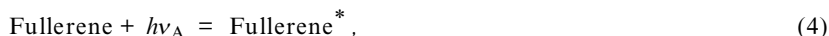


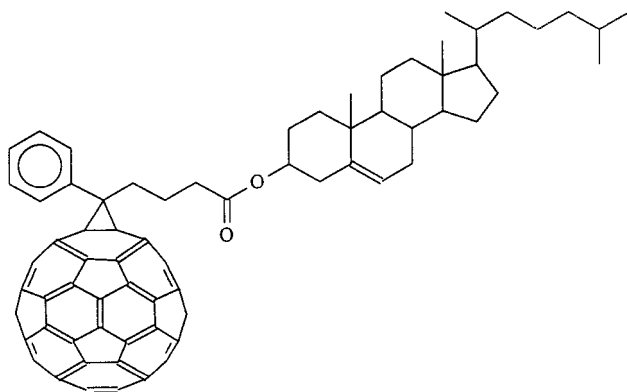
Figure 9. Optical limiting responses (5 ns laser pulses) of C_{60} in room-temperature toluene (\circ) and DEA (∇) solutions of 55% linear transmittance at 532 nm and C_{70} in DEA solution of the same linear transmittance (\square) [109].

responses toward nanosecond laser pulses at 532 nm are much weaker than those in toluene solution [109]. As shown in figure 9, the average saturated output fluence at the optical limiting plateau is 0.21 J cm^{-2} for C_{60} in DEA solution versus 0.05 J cm^{-2} in toluene solution of the same linear transmittance of 55%. For C_{70} in room-temperature toluene, the optical limiting responses are significantly weaker than those of C_{60} . In DEA solution, however, the two fullerene molecules exhibit similar optical limiting responses (figure 9) [109]. The results of C_{60} and C_{70} in DEA or DMA solution have been explained in terms of reverse saturable absorption that is associated with intermolecular electron transfer [109].

It is well established that DEA, DMA, and other aromatic amines undergo intermolecular electron transfers with C_{60} and C_{70} in both ground and excited singlet states [121–129]. The electronic absorption spectra of C_{60} and C_{70} in DEA or DMA solution are different from those in toluene [128]. The stronger ground state absorptions of the fullerenes in aromatic amine solution than in toluene are due to contributions from the fullerene–amine charge transfer complexes. The electron transfers are more efficient in the excited singlet states of the fullerenes. The fluorescence emissions of C_{60} and C_{70} , whose lifetimes in room-temperature toluene are 1.2 ns and 0.6 ns, respectively, are completely quenched in DEA or DMA solution [109, 128]. Thus, upon photoexcitation of C_{60} and C_{70} in DEA, the dominating photo-generated transient species are fullerene radical anion and DEA radical cation [126].



It seems likely that the observed optical limiting responses of C_{60} and C_{70} in solvents of electron donating characteristics such as DEA are dictated by strong absorptions of the fullerene anion radicals generated from the efficient intermolecular electron transfer processes [109]. In this regard, the fullerene–amine systems are in fact



Scheme 4.

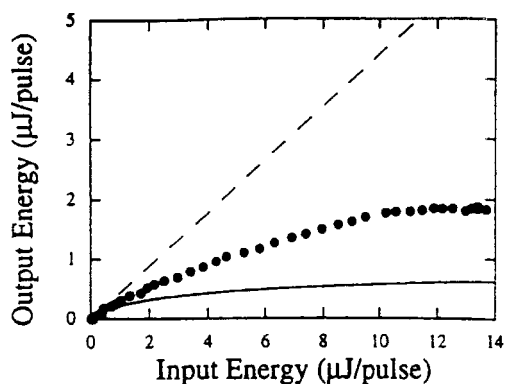


Figure 10. From [77] with the original caption, with permission from the American Institute of Physics. Performance of an optical limiter made of the charge transfer film at 760 nm. Closed circles: experimental data; dashed line: linear transmission line (44%); solid curve: calculated response using the excited cross-section obtained from the Z-scan experiment at low input energy levels.

examples of the intermolecular redox donor–acceptor pairs that are consistent with the SupraRSA concept discussed earlier (figure 8).

Nonlinear absorptions that are associated with strongly absorptive charge separated excited states have also been observed for a C_{60} derivative in poly(3-octylthiophene) film [77]. As reported by Cha *et al.* [77], upon photoexcitation the C_{60} derivative **5** (scheme 4) undergoes charge transfer with poly(3-octylthiophene) polymer in the film to form a fullerene anion radical with a quantum efficiency of near unity. The nonlinearity observed in the fullerene–poly(3-octylthiophene) film at 760 nm is two orders of magnitude greater than that of either one of the two components (figure 10) [77].

Prasad and co-workers reported an interesting experiment in which C_{60} and a second two-photon absorptive optical limiting material were incorporated into the same nanostructured sol–gel composite to provide broadband coverage in optical limiting [65, 66]. In a multi-phase sol–gel glass of excellent optical quality, C_{60} and the second dopant bisbenzothiazole-3,4-didecyloxythiophene, which exhibits

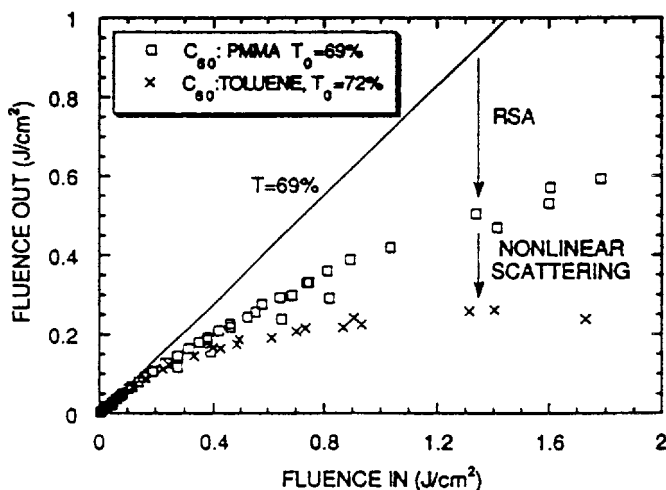


Figure 11. From [67] with the original caption, with permission from the Optical Society of America. Comparison of optical limiting for C_{60} :PMMA with C_{60} :toluene for similarly linear transmitting samples. The liquid appears to have an additional component from nonlinear scattering. RSA, reverse saturable absorption.

characteristic two-photon absorption for nanosecond laser pulses at 800 nm, reside in different phases. The result shows that it is possible to dope two or more optical limiting materials in a solid matrix while retaining the excellent optical quality of the monolithic glass [65, 66].

An intriguing but mechanistically important observation is that the optical limiting responses of C_{60} toward nanosecond laser pulses are dramatically different for the molecule in different media. Generally speaking, the optical limiting performance of C_{60} in a solid state matrix is worse than that in room-temperature solution. For example, it was reported [67] that the optical limiting responses of C_{60} dispersed in a polymethylmethacrylate (PMMA) matrix are significantly weaker than those in room-temperature toluene solution (figure 11). Similarly, weaker optical limiting responses were observed for C_{60} in sol-gel glasses [72, 73, 75]. The results of C_{60} derivatives in different media are similar to those of C_{60} , showing the same kind of dramatic changes in optical limiting performance from room-temperature solution to a polymer matrix (figure 12) [84, 86] or sol-gel glasses [68–71]. The mechanistic reasons behind the experimental observation have been debated in the literature [67, 71, 74]. However, Riggs and Sun recently found [86] that changes in the optical limiting performance of fullerenes are incremental from solution to solid-state matrix. For example, the optical limiting responses of *t*-butyl methano[60]fullerene carboxylate in highly viscous polymer blends such as toluene-PMMA are weaker than those in toluene solution but stronger than those in a PMMA matrix (figures 12 and 13). It implies that the dramatic difference between the optical limiting properties of fullerenes in solution and in solid state polymer matrix is probably due to medium viscosity related effects [86].

For comparison, Riggs and Sun also measured optical limiting responses of the metallophthalocyanine AlClPc as a reference material in a highly viscous DMF-PMMA polymer blend of 70% linear transmittance at 532 nm. Unlike the C_{60} derivative, AlClPc shows the same optical limiting responses in the highly viscous

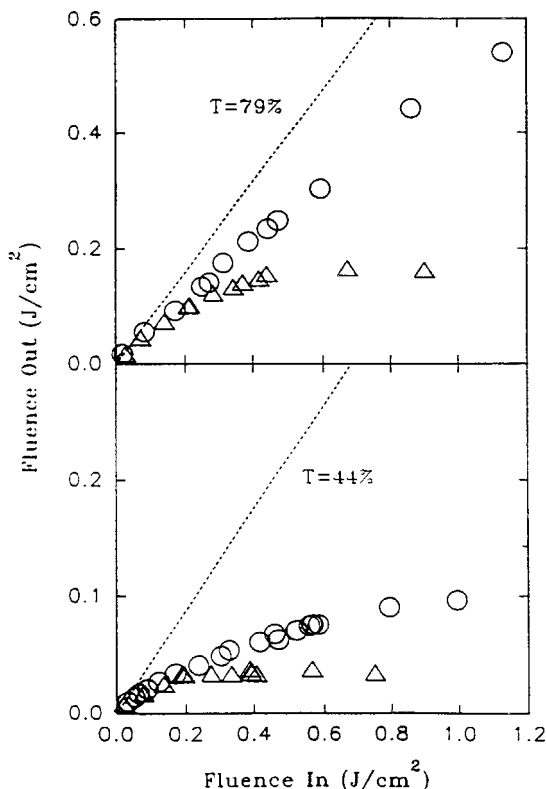


Figure 12. From [84] with the original caption, with permission from the SPIE. Optical limiting responses of the methano- C_{60} derivative **10** in PMMA films (~ 0.4 mm thickness) with linear transmittances of 79% and 44% at 532 nm (\circ). The results of the compound in toluene solutions of the same linear transmittances (\triangle) are also shown for comparison.

polymer blend and in room-temperature DMF solution at the same linear transmittance, namely that the optical limiting properties of AlCIPc are essentially unaffected by the presence of large quantities of PMMA polymer in the DMF solution [86].

3.2. Fullerene derivatives and polymers

Much effort has been made to exploit the possibility of improving the optical limiting performance of C_{60} through cage functionalizations and through the incorporation of fullerene cages into polymeric structures. An additional motivation for studying the optical limiting properties of fullerene derivatives is to improve the processability of fullerene based materials. Generally speaking, fullerene derivatives have much better solubility characteristics than the parent fullerene molecules. For example, it was shown that C_{60} derivatives are better suited in the preparation of fullerene-containing sol-gel glasses for optical limiting applications [68–71].

Among earlier optical limiting investigations of fullerene derivatives is the work by McBranch and co-workers [76]. It was reported that the optical limiting performance of the C_{60} derivative **5** is only slightly worse than that of the parent C_{60} at 532 nm (figure 14), even though the ground state absorption cross-section of the derivative is significantly higher and the excited triplet state absorption of

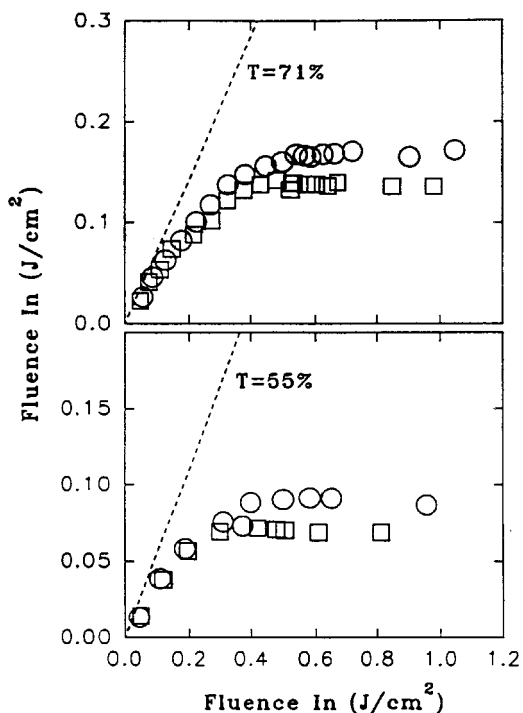


Figure 13. From [86] with the original caption (reprinted with permission from [86]. © 1999 American Chemical Society). Optical limiting responses of the methano- C_{60} derivative **10** in highly viscous toluene-PMMA polymer blends (\circ) with 0.25 g ml^{-1} PMMA at 71% linear transmittance and 0.4 g ml^{-1} at 55% linear transmittance are compared with those in toluene solutions (\square) of the same linear transmittances.

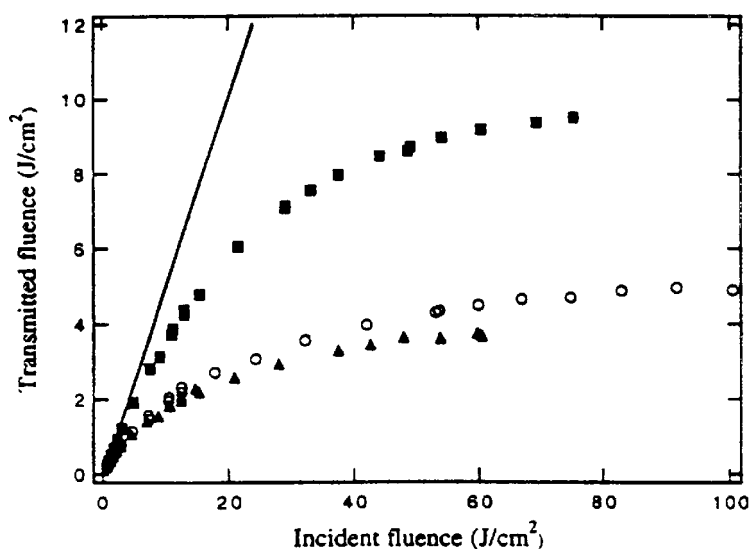
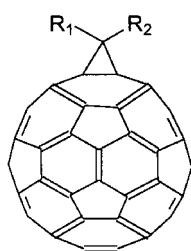
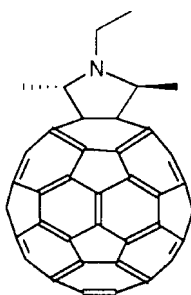


Figure 14. From [76] with the original caption, with permission from the Optical Society of America. Intensity-dependent transmission at 532 nm for C_{60} (Δ), 6,6 PCBCR, **5** (\circ), and 5,6 PCBCR (\blacksquare). The low intensity transmission for each sample is 50%.



- 6:** $R_1=H, R_2=COCN$
7: $R_1=H, R_2=COOEt$
8: $R_1=H, R_2=COPh$
9: $R_1=H, R_2=COC(CH_3)_2CH_2COOEt$
10: $R_1=H, R_2=COOC(CH_3)_3$
11: $R_1=H, R_2=COOH$
12: $R_1=H, R_2=CONEt_2$
13: $R_1=R_2=COOEt$
14: $R_1=R_2=COOH$

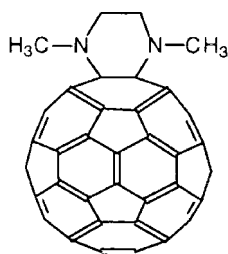
Scheme 5.



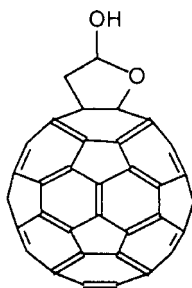
Scheme 6.

the derivative is comparable to that of C_{60} . Recently, Sun and co-workers carried out a systematic investigation of different classes of C_{60} derivatives to compare their optical limiting properties [80–84]. The mono-functionalized fullerenes included in the investigation are methano- C_{60} (**6–14**, see scheme 5), pyrrolidino- C_{60} (**15**, scheme 6), amino- C_{60} (**16**, scheme 7), and other C_{60} derivatives (**17**, scheme 8) [80–82]. The C_{60} dimer (**18**, scheme 9), which may be considered as a linked pair of mono-functionalized C_{60} cages has also been studied [83].

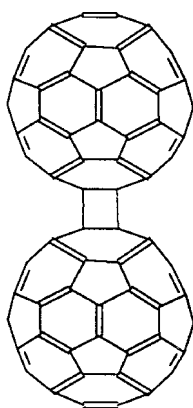
Interestingly, the optical limiting properties of the different classes of C_{60} derivatives with a mono-functionalized fullerene cage are not only nearly identical among themselves but also essentially the same as those of C_{60} in room-temperature solution. For example, the optical limiting responses of the C_{60} derivatives in solutions of 55% and 70% linear transmittances at 532 nm are rather similar, and the results are also similar to those of C_{60} in toluene at the same linear transmittances [80–82].



Scheme 7.



Scheme 8.



Scheme 9.

A more complete summary of optical limiting parameters for the different classes of C_{60} derivatives is provided in table 2. Also shown in table 2 are photophysical parameters of the C_{60} derivatives, which are again similar among the different classes of mono-functionalized fullerenes. However, the C_{60} -dimer **18** is clearly an exception, despite the fact that the dimer may be considered as a pair of mono-functionalized C_{60} cages. As shown in table 2, the optical limiting responses of the C_{60} -dimer are noticeably weaker than those of C_{60} in toluene at 532 nm. The result was explained in terms of weaker triplet-triplet absorption in the dimer than in C_{60} [83].

There are only a handful of experimental investigations on the electronic transitions and excited state properties of C_{60} derivatives with multiple cage functionalizations. Guldi and co-workers reported [130, 131] that bis- and tris-functionalized methano- C_{60} dicarboxylates have different excited triplet state properties from those of C_{60} and the mono-functionalized methano- C_{60} dicarboxylate. There are significant blue-shifts and absorptivity changes in the triplet-triplet absorption as a result of the multiple cage functionalizations. For example, the triplet absorption spectral maximum of the unsymmetric tris-functionalized dicarboxylate derivative peaks at 650 nm, which is ~ 100 nm blue-shifted from that of the parent C_{60} in room-temperature toluene [130, 131]. The blue-shift in triplet-triplet absorption due to multiple cage functionalizations is in principle beneficial to the nonlinear absorption at 532 nm, even though the spectral shift is accompanied by a decrease in the triplet-triplet absorption cross-section [130, 131]. The report prompted Sun and

Table 2. Optical limiting properties of C₆₀ derivatives in room-temperature solution.

Sample	Solvent	τ_f (ns)	I_{OUT} at saturation (Jcm ⁻²) ^a					
			$T = 55\%$	$T = 65\%$	$T = 70\%$	$T = 72\%$	$T = 74\%$	$T = 82\%$
C ₆₀	Toluene	1.2	0.055	0.06	0.1	0.12	0.13	0.18
6	Toluene	1.51	0.065		0.11			
7	Toluene	1.49	0.06		0.1			
7	Dichlorobenzene		0.07		0.12			
7	CHCl ₃		0.06		0.12			
8	Toluene	1.47	0.06		0.12			
9	Toluene	1.46	0.06		0.11			
10	CHCl ₃	1.49	0.06		0.11			
11	CHCl ₃ + 10% DMSO	1.46	0.06		0.11			
12	CHCl ₃	1.45	0.06		0.11			
13	CHCl ₃	1.48	0.06		0.1			
14	THF		0.07		0.12			
15	Toluene	1.5		0.07				0.19
16	Toluene	1.3	0.06			0.13		
17	Toluene	1.6				0.12 ₅		
18	Toluene						0.24	

^a Optical limiting results obtained using a cell of 2 mm optical path length.

co-workers to examine the optical limiting properties of a series of multiple functionalized methano-C₆₀ dicarboxylates in room-temperature solution [132]. As shown in figure 15, the optical limiting responses of the multiple functionalized methano-C₆₀ dicarboxylates **19–21** (schemes 10–12) toward nanosecond laser pulses are all weaker than those of the parent C₆₀ and the mono-functionalized methano-C₆₀ dicarboxylate.

Recently there has been much effort to covalently incorporate fullerene cages into polymers [43, 133, 134]. The changes in fullerene structures due to polymerization are considerably more pronounced than those due to simple derivatizations. Effects of such changes on the optical limiting properties of fullerenes have been investigated by several research groups [78, 79, 84, 85].

Kojima *et al.* reported a study concerning the optical limiting behaviour of the C₆₀-styrene copolymers prepared under high pressure conditions (figure 16) [78 (a)]. Since the copolymers thus prepared are insoluble, the optical limiting measurements were performed in the solid state, which probably prevented a direct comparison between the copolymers and the parent C₆₀ for optical limiting under the same conditions. The results are somewhat ambiguous with respect to the question of any improvement in the optical limiting performance upon the copolymerization of C₆₀ cages with styrene molecules [78]. Recently, Tang *et al.* made a claim [79] that some fullerene-containing polymers of aromatic and chlorine moieties including C₆₀-polycarbonate, C₆₀-polystyrene, and C₆₀-poly(vinyl chloride) polymers limit 8 ns laser pulses at 532 nm more effectively than does the parent C₆₀. It was implied that the improved optical limiting performance in the polymers may be attributed to larger σ_T/σ_G ratios in polymer-bound fullerenes, although there was no experimental determination of even ground state absorption cross-sections of the fullerene-containing polymers in a quantitative fashion [79]. Without any information on the degree of cage functionalizations in the polymer-bound fullerenes,

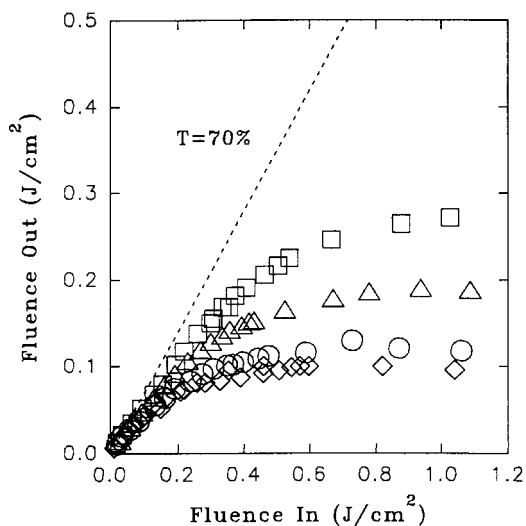
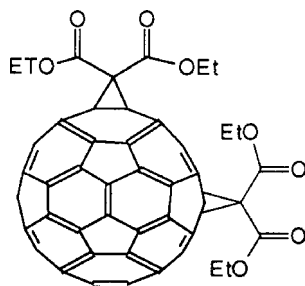
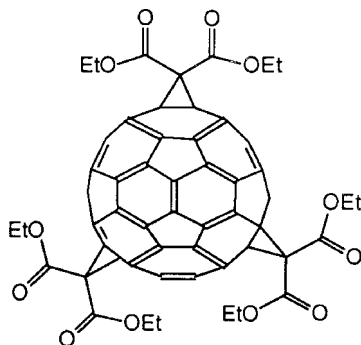


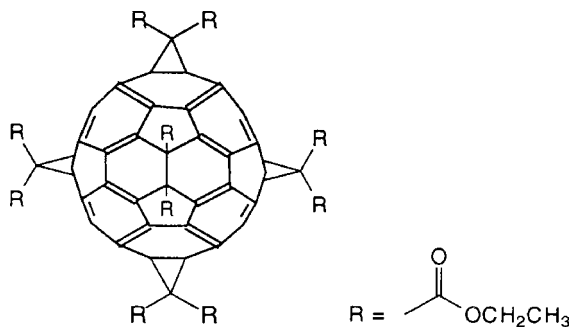
Figure 15. Optical limiting responses (5 ns laser pulses) of the bis-functionalized methano- C_{60} dicarboxylate **19** in toluene (\circ), the symmetric tris-functionalized methano- C_{60} dicarboxylate **20** in toluene (\square), and the hexakis-functionalized methano- C_{60} dicarboxylate **21** in chloroform (\triangle) are compared to those of C_{60} in toluene (\diamond) at 70% linear transmittance at 532 nm [132].



Scheme 10.



Scheme 11.



Scheme 12.

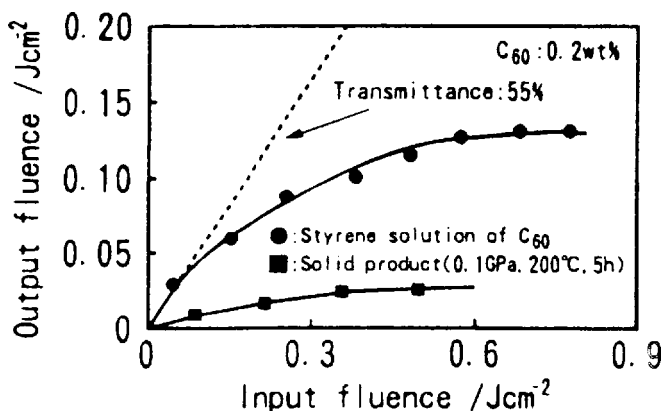
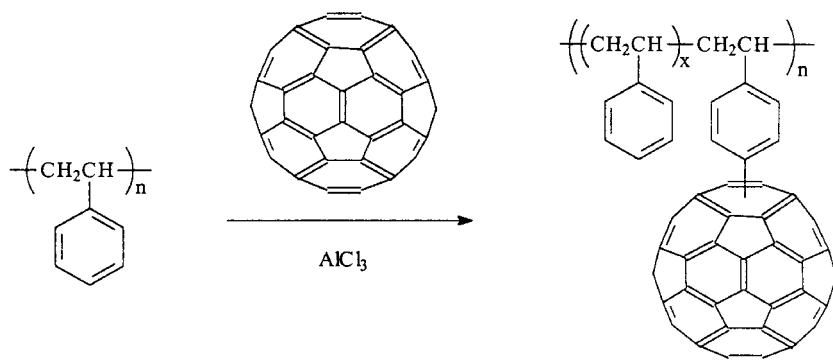


Figure 16. From [78 (a)] with the original caption (reprinted with permission from [78 (a)]. © 1995 American Chemical Society). Relationship between output fluence and input fluence of the solid product with polystyrene-bound C_{60} together with the solution of C_{60} in styrene (path length for the solution: 1 mm).

it seems difficult to assess the actual effects on the ground state absorption cross-section of C_{60} upon the incorporation of the cages into polymeric structures. For C_{60} -styrene and C_{60} -PMMA copolymers prepared by several research groups [135–139], however, the ground state absorption of the copolymers at 532 nm is definitely stronger than that of the parent C_{60} on a per cage basis [138, 140].

The optical limiting properties of the fullerene-containing polymers must be very sensitive to the methods and experimental conditions used in the polymer preparation if the polymeric materials of Tang *et al.* are indeed better optical limiters than the parent C_{60} . The C_{60} -styrene copolymers obtained by Sun and co-workers [137, 138] are apparently very different, exhibiting much worse optical limiting performance than the parent C_{60} toward nanosecond laser pulses at 532 nm [140]. In fact, the optical limiting responses of the C_{60} -styrene copolymers with C_{60} contents from 0.08% to ~50% (wt/wt) are very weak (table 3). Similarly poor optical limiting results were obtained for the poly- C_{60} (table 3) [83], which is a polymer of covalently linked C_{60} cages prepared in a photopolymerization reaction [141]. In order to have a mechanistic understanding of the optical limiting results, Sun and co-workers conducted a careful laser flash photolysis investigation of the



Scheme 13.

Table 3. Optical limiting properties of C₆₀ containing polymers in room-temperature solution.

Sample	Solvent	I_{OUT} at saturation ($J\text{ cm}^{-2}$) ^a		
		$T = 55\%$	$T = 60\%$	$T = 70\%$
C ₆₀	Toluene	0.055	0.057	0.1
Pendent C ₆₀ -polystyrene ^b	Chloroform	0.07		0.15
C ₆₀ -styrene copolymer ^c	Chloroform	0.20		0.30
Poly-C ₆₀	DMSO		0.26 ^d	

^a Optical limiting results obtained using a cell of 2 mm optical path length.

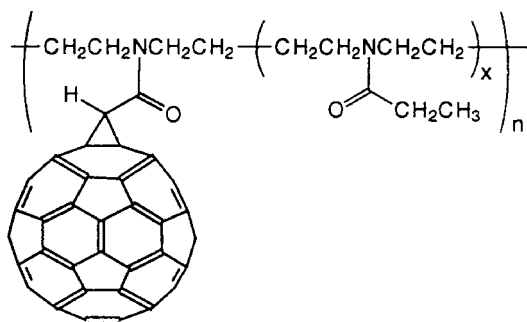
^b M_W of $\sim 10\,000$ and C₆₀ content of $\sim 10\%$ (wt/wt).

^c Contains C₆₀ content of $\sim 14\%$ (wt/wt).

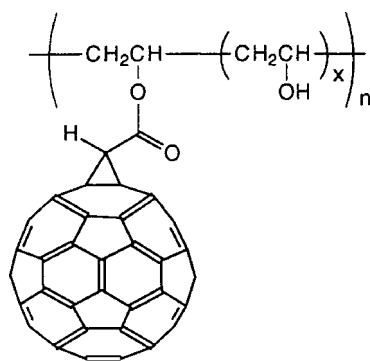
^d The value at I_{IN} of 0.8 J cm^{-2} . No plateau is reached.

C₆₀-styrene copolymers [140] and the poly-C₆₀ polymer [83]. The triplet-triplet absorption spectra of the copolymers with C₆₀ contents of 0.4 and 30% (wt/wt) in room-temperature toluene solution are an order of magnitude weaker than those of the parent C₆₀ and mono-functionalized C₆₀ derivatives [140]. The results are similar to those obtained earlier by Kamat *et al.* for the same C₆₀-styrene copolymers [142]. For the poly-C₆₀ in a carefully deoxygenated dimethylsulphoxide (DMSO) solution under the same experimental conditions as those for the parent C₆₀ and the C₆₀-dimer (**18**), the transient absorption signals were too weak to be distinguished clearly from the noise. It was concluded [83] that the triplet state absorption in the poly-C₆₀ polymer is weaker than those in the parent C₆₀ and the C₆₀-dimer by at least an order of magnitude. Thus, it is no surprise that the C₆₀-styrene copolymers and the poly-C₆₀ polymer have poor optical limiting properties [83, 140].

Sun and co-workers also investigated the optical limiting properties of pendant fullerene-polystyrene polymers **22** (scheme 13), in which C₆₀ cages are attached to the phenyl groups in polystyrene [84, 85]. The optical limiting responses of the pendant polymers toward nanosecond laser pulses at 532 nm are much better than those of the C₆₀-styrene copolymers (table 3), but still not as good as those of the parent C₆₀ and mono-functionalized C₆₀ derivatives [80-85]. Due to multiple functionalizations of some fullerene cages, there are likely various degrees of crosslinking among pendant



Scheme 14.

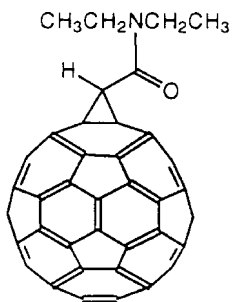


Scheme 15.

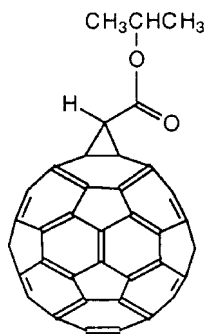
fullerene-polystyrene polymer species. However, it was shown that the possible crosslinking hardly affects the optical limiting properties of the fullerene-containing polymers [85].

Pendant fullerene polymers are structurally better defined [133,134,143–151] and therefore allow more reproducible investigations of optical limiting properties of polymer-bound fullerenes. Sun and co-workers have also examined pendant methano- C_{60} -poly(propionylethyleneimine) (MFCA-PPEI, **23**, scheme 14) and pendant methano- C_{60} -poly(vinyl alcohol) (MFCA-PVA, **25**, scheme 15) in homogeneous solution for their optical limiting responses toward nanosecond laser pulses at 532 nm [152]. The pendant fullerene polymers exhibit poorer optical limiting performance than the parent C_{60} and the methano- C_{60} derivatives **24** (scheme 16) and **26** (scheme 17), which serve as monomeric models for the pendant fullerene polymers. For example, as compared in figure 17, the optical limiting responses of the pendant MFCA-PPEI polymer are weaker than those of the model compound **24** [152]. However, it will be discussed below that the optical limiting of monomeric fullerene molecules in solution is likely contributed by bimolecular processes [86]. For polymer-bound fullerenes, bimolecular processes are obviously more difficult, which might be partially responsible for the poorer optical limiting performance of the pendant fullerene polymers in solution.

There are still many issues to be addressed concerning the optical limiting properties of fullerene-containing polymers. However, it appears that unless completely different mechanisms are invoked upon the incorporation of fullerene cages into



Scheme 16.



Scheme 17.

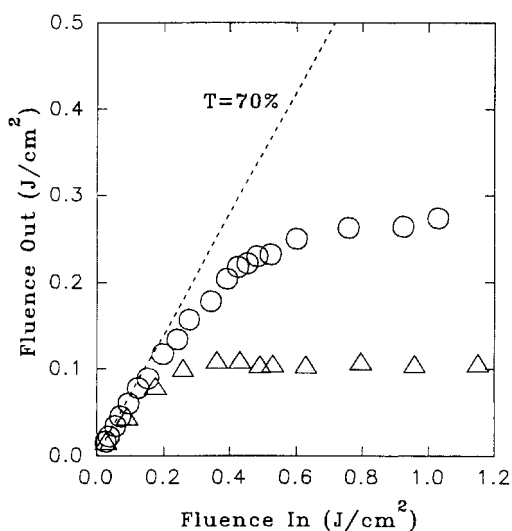


Figure 17. Optical limiting responses (5 ns laser pulses) of the pendant MFCA-PPEI polymer **23** with $\sim 8\%$ C₆₀ content in chloroform solution of 70% linear transmittance at 532 nm (○) are compared with those of the model compound **24** obtained under the same experimental conditions (△) [152].

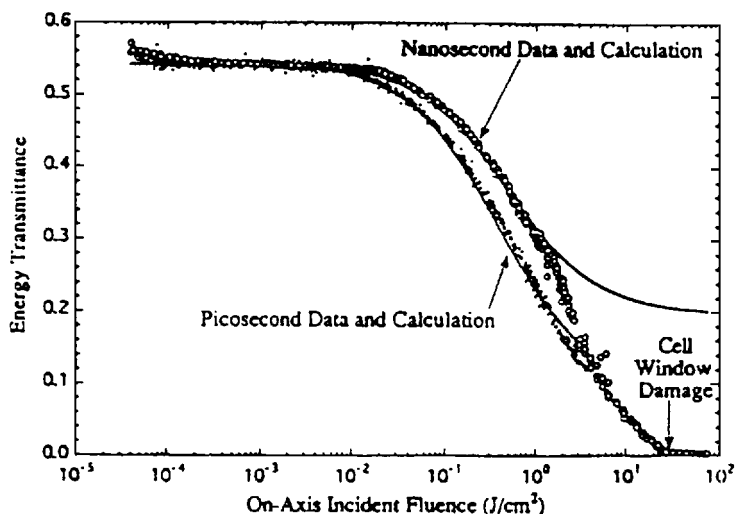


Figure 18. From [61] with the original caption, with permission from the Optical Society of America. Energy transmittance of a 2.59 mM C_{60} -toluene solution in a 1 mm cuvette as a function of on-axis incident fluence for 8 ns (\circ) and 30 ps (\bullet) 532 nm laser pulses. The solid curves are theoretical calculations for the two data sets based on a five level model described in the text.

polymer structures, the potential for improving optical limiting performance of fullerenes through polymerization is probably limited.

3.3. Optical limiting mechanism

Optical limiting properties of fullerenes have been explained in terms of the five-level reverse saturable mechanism (figure 2(a)). For example, McLean *et al.* used the five-level model to correlate observed optical limiting responses of C_{60} in room-temperature toluene solution with the ground and excited state absorption cross-sections of C_{60} [44, 61]. For limiting nanosecond laser pulses at 532 nm, there is a nearly quantitative agreement between the experimental results and the five-level model for input light fluences of up to $\sim 1 \text{ J cm}^{-2}$ (figure 18). The nearly quantitative agreement in the correlation lends strong support to the reverse saturable absorption mechanism for optical limiting in fullerenes. Similar correlations were performed by several other groups [47, 153], which yielded results that are in general also supportive to the reverse saturable absorption mechanism.

With the fact that both the excited singlet and triplet state absorption cross-sections are larger than the ground state absorption cross-section for C_{60} in room-temperature toluene [61], there seems no doubt that nonlinear absorption contributes to the observed optical limiting responses of C_{60} . The intersystem crossing yield of C_{60} is unity and the triplet state rise time should be the same as the fluorescence lifetime of 1.2 ns [43, 154]. Thus, the nonlinear absorptive optical limiting of nanosecond laser pulses by C_{60} is due predominantly to stronger excited triplet state absorption than the ground state absorption, $\sigma_T/\sigma_G > 1$. Because the triplet-triplet absorption spectrum of C_{60} peaks at $\sim 740 \text{ nm}$ [155], the nonlinear absorptions are stronger at longer visible wavelengths. This is reflected in the optical limiting results of C_{60} at different wavelengths. However, the question remains whether reverse sat-

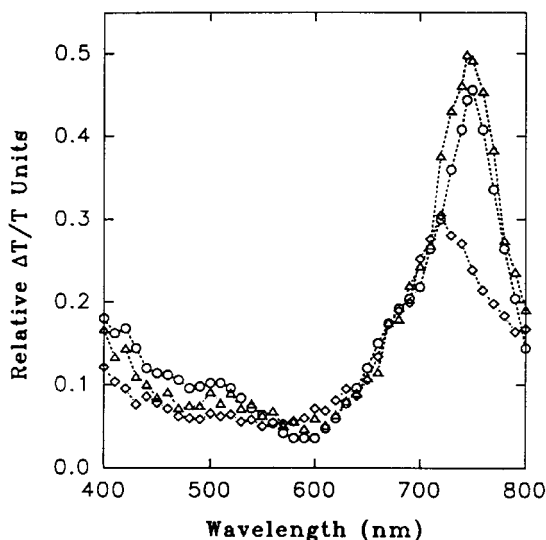


Figure 19. The triplet-triplet absorption spectrum of the methano- C_{60} derivative **10** (\diamond) is compared with those of C_{60} (Δ : [83] and \circ [153(a)]). (Reprinted with permission from [86]. © 1999 American Chemical Society.)

urable absorption is the only mechanism or, at least, the dominant mechanism for the optical limiting properties of fullerenes. In fact, there are suggestions of other optical limiting mechanisms [49, 63, 64, 67]. For example, it has been proposed that the optical limiting responses of C_{60} consist of significant contributions from other nonlinear optical processes such as nonlinear scattering [49, 63, 67]. The search for alternative mechanisms or substantial contributions from mechanisms other than the reverse saturable absorption has been prompted by some inconsistencies between the expectations on the basis of reverse saturable absorption and the experimental optical limiting results of C_{60} and derivatives. Among the most important experimental evidence for the possibility of other mechanisms is that the optical limiting performance of fullerenes in solid matrices is dramatically different from that in solution, as discussed in the previous section. The weakening in optical limiting responses of fullerenes from solution to solid matrices cannot be explained within the framework of reverse saturable absorption, which is associated with a large σ_T/σ_G ratio (figure 2(c)), because the triplet-triplet absorption spectrum of C_{60} undergoes only minor changes from toluene solution to PMMA polymer film [156]. Similarly, the medium viscosity dependence of the optical limiting responses of C_{60} and the methano- C_{60} derivative observed by Riggs and Sun [86] can hardly be accounted for using only the reverse saturable absorption mechanism.

The reverse saturable absorption mechanism alone also does not account for the optical limiting results of C_{60} and mono-functionalized C_{60} derivatives quantitatively and consistently. For the methano- C_{60} derivative **10**, the intersystem crossing yield is unity according to the result of photosensitization for singlet molecular oxygen generation [157]. Based on the results obtained by Riggs and Sun [86], the derivative has the absorption cross-section ratio $\sigma_T/\sigma_G > 1$, satisfying the requirement for reverse saturable absorption. More quantitatively, however, the ground state absorption cross-section of the derivative is larger than that of C_{60} ($4.78 \times 10^{-18} \text{ cm}^2$ versus $3.59 \times$

10^{-18} cm^2 at 532 nm), and the triplet–triplet absorption cross-section of the derivative is smaller than that of C_{60} at 532 nm (figure 27). Thus, $(\sigma_{\text{T}}/\sigma_{\text{G}})_{\text{DERIVATIVE}} < (\sigma_{\text{T}}/\sigma_{\text{G}})_{\text{C}_{60}}$, which would suggest weaker optical limiting responses for the derivative. The experimental results obtained by Riggs and Sun [86] show otherwise. The optical limiting responses of the methano- C_{60} derivative **10** in a room-temperature toluene solution of $6.16 \times 10^{-4} \text{ M}$ concentration (2 mm optical path length and 70% linear transmittance) are close to those of C_{60} obtained under comparable conditions [86]. Similar concerns were expressed by McBranch and co-workers in the comparison of optical limiting results of the C_{60} derivative **5** and the parent C_{60} [76]. The similarity in optical limiting performance between the parent C_{60} and C_{60} derivatives seems to suggest that observed optical limiting responses of fullerenes are dominated by contributions that are not so sensitive to the difference in $\sigma_{\text{T}}/\sigma_{\text{G}}$ ratios.

A further complication is due to the fact that the optical limiting results of C_{60} and derivatives in room-temperature solution were found to be strongly dependent on solution concentrations [86]. Wray *et al.* first examined effects of concentration on the optical limiting performance of C_{60} in solution [50]. The results from optical limiting measurements of C_{60} in toluene solution over a relatively narrow concentration range (1×10^{-4} to $4 \times 10^{-4} \text{ M}$) show some variations, although the variations appear to be within the margins associated with the relatively large experimental uncertainties [50]. Nevertheless, it was concluded [50, 51] that the clamped level of the output fluence at the optical limiting plateau is determined by the amount of C_{60} in the beam path, namely that the optical limiting responses of C_{60} in solution are concentration independent. Riggs and Sun recently re-examined the issue of solution concentration dependence through a systematic experimental investigation of optical limiting in room-temperature solutions of C_{60} and the methano- C_{60} derivative **10** with concentrations varying over a wide range (6.16×10^{-3} to $1.23 \times 10^{-5} \text{ M}$ for the derivative **10**) [86]. In the optical limiting measurements, the linear transmittance of the solutions was kept constant at 70% through the use of optical cuvettes of different path lengths. As shown in figures 20 (a) and (b), the results suggest that the optical limiting responses of C_{60} and the methano- C_{60} derivative in room-temperature solutions are strongly concentration dependent. For example, for the methano- C_{60} derivative at a high concentration of $6.16 \times 10^{-4} \text{ M}$, an optical cell of 2 mm path length was used to maintain the linear transmittance at 70%. The concentrated solution exhibits strong optical limiting responses, reaching a plateau at an input fluence of $\sim 0.33 \text{ J cm}^{-2}$, and the average saturated output fluence at the optical limiting plateau is $\sim 0.11 \text{ J cm}^{-2}$ (figure 20 (a)). The results of more dilute solutions are very different, with significantly larger saturated output fluence values or even without reaching a plateau region at all (figure 20 (a)). Interestingly, however, the concentration dependence of optical limiting disappears at very low fullerene concentrations. For the methano- C_{60} derivative in toluene, the optical limiting responses become significantly weaker when the solution concentration is reduced from $6.16 \times 10^{-5} \text{ M}$ (20 mm optical path length) to $2.46 \times 10^{-5} \text{ M}$ (50 mm optical path length), but remain essentially the same when the solution concentration is reduced further by a factor of 2 from $2.46 \times 10^{-5} \text{ M}$ to $1.23 \times 10^{-5} \text{ M}$ (figure 20 (a), table 4). It was thus concluded [86] that the threshold concentration for the concentration dependence of optical limiting is in the 2.46×10^{-5} to $6.16 \times 10^{-5} \text{ M}$ range for the methano- C_{60} derivative **10** in room-temperature toluene.

According to figure 20 (b), the changes in optical limiting responses of C_{60} are relatively small over the narrow concentration range of 1×10^{-4} to $4 \times 10^{-4} \text{ M}$ used in

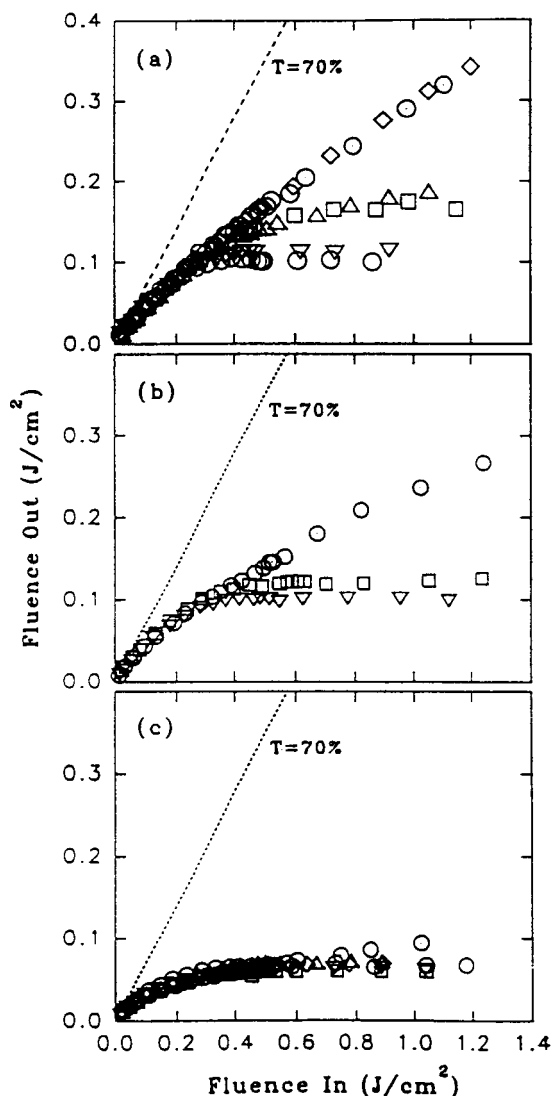


Figure 20. Optical limiting responses of (a) the methano- C_{60} derivative **10** and (b) C_{60} in toluene and (c) AIClPc in DMF at room temperature toward 5 ns laser pulses in a collimated beam geometry. At a constant linear transmittance of 70% at 532 nm, the solution concentration decreases with the optical path length (\odot : 1 mm, ∇ : 2 mm, \square : 10 mm, \triangle : 20 mm, \odot : 50 mm, and \diamond : 100 mm). (Reprinted with permission from [86]. © 1999 American Chemical Society.)

the earlier study [50, 51], so that the concentration dependence of optical limiting is not so obvious. The study by Riggs and Sun [86] benefited from the inclusion of more dilute solutions (1.23×10^{-5} to 6.16×10^{-5} M) in the optical limiting measurements. It is in the low concentration region that optical limiting responses of the fullerenes exhibit significant variations with changes in the solution concentration (figure 20 (a) and (b)). However, despite the fact that the different results and conclusions from the different laboratories [50, 51, 86] seemed explainable, Riggs and Sun were still deeply

Table 4. Optical limiting properties of C₆₀ and methano-C₆₀ derivative **10** in solution and in highly viscous solvent-polymer blends.

<i>c</i> (M)	Solvent	<i>l</i> (mm) ^{<i>a</i>}	<i>T</i> (532 nm)	<i>I</i> _{OUT} (J cm ⁻²) ^{<i>b</i>}	<i>T</i> / <i>T</i> ₀ ^{<i>b</i>}
C ₆₀					
3.28 × 10 ⁻⁵	Toluene	50	70%	0.23 ₅	0.34
1.64 × 10 ⁻⁴	Toluene	10	70%	0.23	0.17
8.19 × 10 ⁻⁴	Toluene	2	70%	0.1	0.14
Methano-C ₆₀ derivative					
1.23 × 10 ⁻⁵	Toluene	100	70%	0.30 ₅	0.44
2.46 × 10 ⁻⁵	Toluene	50	70%	0.3	0.43
6.16 × 10 ⁻⁵	Toluene	20	70%	0.18	0.26
1.23 × 10 ⁻⁴	Toluene	10	70%	0.17	0.24
6.16 × 10 ⁻⁴	Toluene	2	70%	0.11	0.16
1.23 × 10 ⁻³	Toluene	1	70%	0.1	0.14
6.16 × 10 ⁻³	Toluene	0.2	69%	0.09 ₅	0.13 ₇
5.92 × 10 ^{-4c}	Toluene-PMMA ^{<i>d</i>}	2	71%	0.17	0.24
5.92 × 10 ⁻⁴	Toluene	2	71%	0.14	0.2
1.04 × 10 ^{-3c}	Toluene-PMMA ^{<i>e</i>}	2	55%	0.09	0.16
1.04 × 10 ⁻³	Toluene	2	55%	0.07	0.13
6.4 × 10 ^{-4c}	CHCl ₃ -PPEI ^{<i>f</i>}	2	69%	0.16	0.23
6.4 × 10 ⁻⁴	Toluene	2	69%	0.1	0.15

^{*a*} Optical path length.

^{*b*} At *I*_{IN} = 1 J cm⁻².

^{*c*} Estimated with the assumption of the same molar absorptivity as in toluene.

^{*d*} Contains 0.25 g ml⁻¹ of PMMA.

^{*e*} Contains 0.4 g ml⁻¹ of PMMA.

^{*f*} Contains 0.3 g ml⁻¹ of poly(propionylethyleneimine) (PPEI).

concerned about the possibility of instrumental artefacts or special optical effects in the experiments for optical limiting measurements, particularly with the use of long path length optical cells (50 and 100 mm). In this regard, the comparison of the optical limiting results obtained using short path length optical cells, especially those with 0.2 and 2 mm optical path lengths [158] (table 4), provides more convincing support to the conclusion that the optical limiting responses of the fullerenes in solution are indeed strongly concentration dependent [86].

A direct comparison between the results of the fullerenes and the metallophthalocyanine AICIPc provides additional support to the conclusion of concentration dependent optical limiting of fullerenes. Riggs and Sun used AICIPc as a reference for optical limiting measurements under the same experimental conditions as those for C₆₀ and the methano-C₆₀ derivative **10**. A series of solutions of AICIPc in DMF at different concentrations from 2.7 × 10⁻⁵ to 2.7 × 10⁻³ M were used in the measurements [86]. With optical cuvettes of different path lengths, the linear transmittance of the AICIPc solutions was kept constant at 70% at 532 nm. As shown in figure 20 (c), optical limiting responses of AICIPc are hardly solution concentration dependent. The saturated output fluence values at the optical limiting plateau are around 0.06 J cm⁻² for all of the AICIPc solutions (figure 20 (c)). Obviously, the results are very different from those of the fullerenes [86].

With the optical limiting results of C₆₀, the methano-C₆₀ derivative, and AICIPc

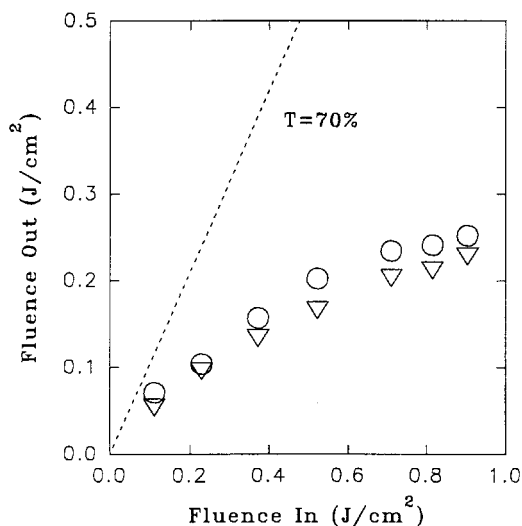


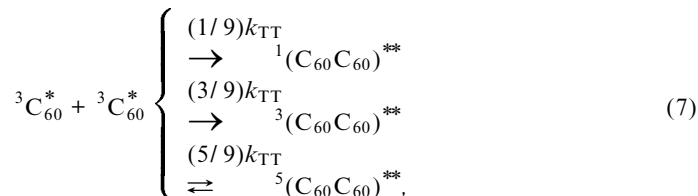
Figure 21. Optical limiting responses of the methano-C₆₀ derivative **10** in room-temperature toluene solutions of different concentrations toward 80 ps laser pulses in a collimated beam geometry at 532 nm. Optical cells of 2 cm (▽) and 0.2 mm (○) path lengths were used to keep the solution linear transmittance constant at 70% [158].

obtained under various conditions, it seems inevitable to conclude that optical limiting properties of the fullerenes in solution are strongly concentration dependent [86]. Mechanistically, concentration dependence in photophysical properties is typically a result of significant involvement of bimolecular processes. The concentration dependence of optical limiting may be treated in a similar fashion. Riggs and Sun proposed [86] that the strongly concentration dependent optical limiting in fullerenes might be an indication of significant optical limiting contributions that are associated with bimolecular processes in the fullerene excited states. Since the bimolecular processes are likely dependent on the medium viscosity, the changes in optical limiting responses of fullerenes from room-temperature solution to highly viscous polymer blends and to solid state matrices may be related to changes in medium viscosity effects on bimolecular processes. The contributions of bimolecular processes are apparently subject to a concentration threshold, which represents the minimum fullerene solution concentration required for the bimolecular excited state processes to be significant with respect to optical limiting toward nanosecond laser pulses. Interestingly, picosecond laser pulses are probably too short-lived to feel the impact of bimolecular processes. As shown in figure 21, the optical limiting responses of the methano-C₆₀ derivative **10** toward 80 ps laser pulses are hardly dependent on the fullerene concentration [158]. According to Riggs and Sun [86], it is below the concentration threshold that optical limiting properties of fullerenes are dominated by the simple five-level reverse saturable absorption mechanism. In this regard, the five-level (figure 2 (a)) or simplified three-level model (figure 2 (c)) for nonlinear absorptive optical limiting may be considered as the unimolecular reverse saturable absorption model for fullerenes. Thus, equations (1)–(3) are effectively differential equations for the unimolecular reverse saturable absorptive optical limiting of fullerenes. Without solution concentration dependent terms, the equations cannot account for any optical limiting contributions from concentration dependent processes [86].

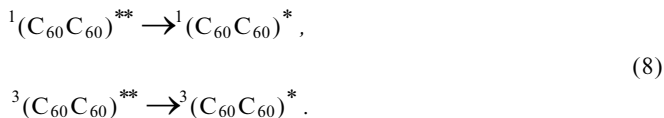
While the bimolecular processes can in principle be associated with both the excited singlet and triplet states of fullerenes, the excited triplet state processes should be more likely or at least more significant. According to results from time-resolved fluorescence investigations, the fluorescence lifetimes of C_{60} and the methano- C_{60} derivative **10** in room-temperature solution are concentration independent over the concentration range used in the study of concentration dependent optical limiting [43, 86, 154, 158]. Thus, the excited singlet state decays of the fullerenes in solution, which are dominated by the efficient intersystem crossing to the formation of excited triplet state, are concentration independent. On the other hand, concentration effects on the excited triplet state properties of fullerenes are well documented. In a series of careful flash photolysis experiments, Weisman and co-workers have shown [159, 160] that the excited triplet state decays and lifetimes of C_{60} and methano- C_{60} derivatives in room-temperature solution are strongly dependent on fullerene concentrations. The strong concentration dependence of excited triplet state properties was attributed to bimolecular processes including self-quenching and triplet-triplet annihilation [159, 160]. Riggs and Sun proposed that the same excited triplet state bimolecular processes may be responsible for the concentration dependent optical limiting of the fullerenes [86]. It was suggested [86] that one possible process might be the formation of a triplet excimer-like state with a large absorption cross-section.



The other possible process might be triplet-triplet annihilation [86, 161].



where the double asterisks denote doubly-excited pairs and k_{TT} is the triplet-triplet annihilation rate constant. The singlet and triplet doubly-excited pairs formed initially from the triplet-triplet annihilation rapidly relax to singlet and triplet excimer-like states [86, 161].



Riggs and Sun suggested [86] that both of these possible contributions may still be accounted for within the framework of nonlinear absorptions due to larger excited state absorption cross-sections than the ground state absorption cross-section. It was proposed [86] that the unimolecular five-level reverse saturable absorption model shown in figure 2(a) may be modified to include the bimolecular excited state processes. Under the assumption that the optical limiting properties of fullerenes are significantly affected by absorptions of the singlet and triplet excimer-like states, the modified reverse saturable absorption model that includes both unimolecular and bimolecular excited state processes in fullerenes may be described by the scheme

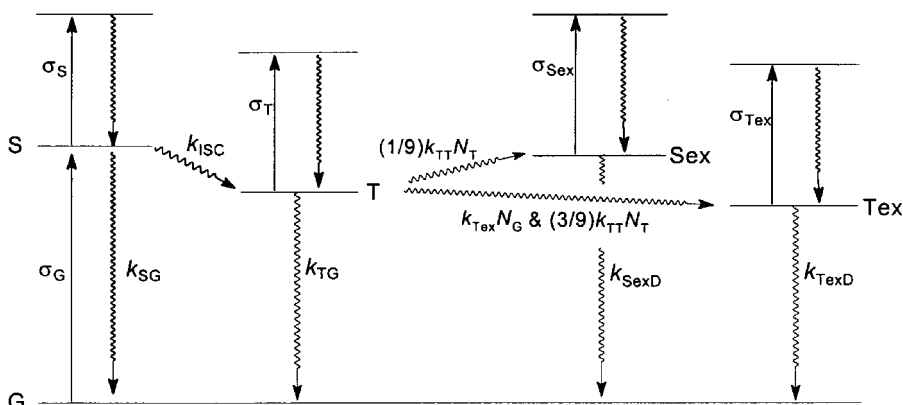


Figure 22. A modified reverse saturable absorption mechanism for fullerenes in solution that includes both unimolecular and bimolecular excited state processes. (Reprinted with permission from [86]. © 1999 American Chemical Society.)

shown in figure 22 [86]. The corresponding differential equations for the modified model are as follows.

$$di/dx = -i(\sigma_G N_G + \sigma_S N_S + \sigma_T N_T + \sigma_{Sex} N_{Sex} + \sigma_{Tex} N_{Tex}), \quad (9)$$

$$dN_S/dt = \sigma_G N_G i - (k_{SG} + k_{ISC})N_S, \quad (10)$$

$$dN_T/dt = k_{ISC}N_S - k_{TG}N_T - (4/9)k_{TT}N_T^2 - k_{Tex}N_T N_G, \quad (11)$$

$$dN_{Sex}/dt = (1/9)k_{TT}N_T^2 - k_{SexD}N_{Sex}, \quad (12)$$

$$dN_{Tex}/dt = k_{Tex}N_T N_G + (3/9)k_{TT}N_T^2 - k_{TexD}N_{Tex}, \quad (13)$$

where the subscripts Sex and Tex denote singlet and triplet excimer-like states, respectively.

The modified reverse saturable absorption model (figure 22) proposed by Riggs and Sun [86] has not been confirmed experimentally. While significant self-quenching of the C_{60} excited triplet state by ground state C_{60} molecules has been observed at moderate solution concentrations [159, 160], no triplet excimer of C_{60} has been detected. However, Riggs and Sun argued [86] that the results from laser flash photolysis measurements are not sufficient to rule out the possibility of an excimer-like state on the time scale of a few nanoseconds. Short-lived complexes of ground and excited triplet state fullerene molecules that are strongly absorptive may be populated under the intense pulsed laser irradiation, contributing to the optical limiting of fullerenes in solution. Similarly for the triplet-triplet annihilation in fullerene solution, while there has been no report of any delayed excited singlet state transient absorption from the bimolecular process, its strong effect on the excited triplet state decays of fullerenes in laser flash photolysis experiments is well documented [159, 160]. Under the condition of high laser power densities in optical limiting measurements, which is much different from that in transient absorption experiments, the triplet-triplet annihilation process should be more significant. In addition to the light intensity, the triplet-triplet annihilation depends on the concentration of ground state fullerene molecules. At a constant linear transmittance in optical limiting measurements, a lower solution concentration corresponds to a longer optical path length, which

makes it less likely to generate a high local concentration of excited triplet fullerene molecules in the laser beam path for efficient triplet–triplet annihilation [86].

Experimentally, observed optical limiting properties of fullerenes are dependent on both the solution concentration and viscosity. Riggs and Sun also suggested [86] that both dependencies may be consistently accounted for within the framework of the modified reverse saturable absorption mechanism shown in figure 22. Since the excited state bimolecular processes are likely diffusional in nature, they are hindered significantly in highly viscous media. In the modified mechanism shown in figure 22, the viscosity effect is reflected in the rate constants of the bimolecular excited state processes (k_{TT} and k_{Tex} , equations (8)–(11)). For fullerenes in polymer films and solid state matrices, diffusional processes on the nanosecond time scale become essentially impossible. Thus, according to Riggs and Sun [86], the absence of any optical limiting contributions that are associated with excited triplet state bimolecular processes may be responsible for the much weaker optical limiting responses of C_{60} and derivatives in polymer films and solid state matrices. It was further suggested [86] that the optical limiting results in polymer films and solid state matrices may in fact reflect the true unimolecular reverse saturable absorption behaviour of fullerenes, which follows the unimolecular five-level mechanism shown in figure 2(a). The suggestion is supported by two pieces of experimental evidence. One is that the optical limiting responses of the methano- C_{60} derivative **10** in thin (<0.1 mm) and thick (~ 0.4 mm) PMMA films of the same linear transmittance are indistinguishable, despite the fact that the film thicknesses (or the optical path lengths) differ by more than a factor of 4 [86]. The other is the plot shown in figure 23. For the methano- C_{60} derivative **10** in a series of PMMA polymer films of the same thickness (0.4 mm) but varying linear transmittances, the output fluences corresponding to the constant input fluence of 1 J cm^{-2} ($I_{OUT,IN=1}$) are different, decreasing monotonically with decreasing linear transmittance of the films. The relationship between $I_{OUT,IN=1}$ and the linear transmittance is apparently well represented by a smooth curve (figure 23). On the other hand, for the derivative in toluene solutions of a constant 70% linear transmittance at 532 nm, $I_{OUT,IN=1}$ increases steadily with decreasing solution concentration (figure 23). The data points corresponding to the low solution concentrations, that are at or below the threshold for concentration dependence of optical limiting, fall right on the smooth curve for the optical limiting results of the derivative in PMMA polymer films (figure 23). A conclusion from the plot in figure 23 is that the optical limiting behaviour of the fullerene in PMMA polymer films is close to that in room-temperature solution in the absence of effects associated with the concentration dependent bimolecular excited state processes [86]. According to Riggs and Sun [86], the excited triplet state bimolecular processes in the modified reverse saturable absorption model shown in figure 22 are absent for fullerenes in polymer films due to the lack of molecular diffusion and also absent in dilute solutions because the concentrations are too low to support meaningful bimolecular processes on the excited state time scale. Under such conditions, the modified mechanistic model shown in figure 22 becomes equivalent to the simple unimolecular five-level reverse saturable absorption model shown in figure 2(a).

The observation of strong concentration dependence of optical limiting in fullerenes is important to potential applications of the materials and to the mechanistic elucidation of the optical limiting properties. Riggs and Sun tried to explain qualitatively all of the available experimental results in a consistent fashion by proposing a modified reverse saturable absorption model (figure 22) [86]. However,

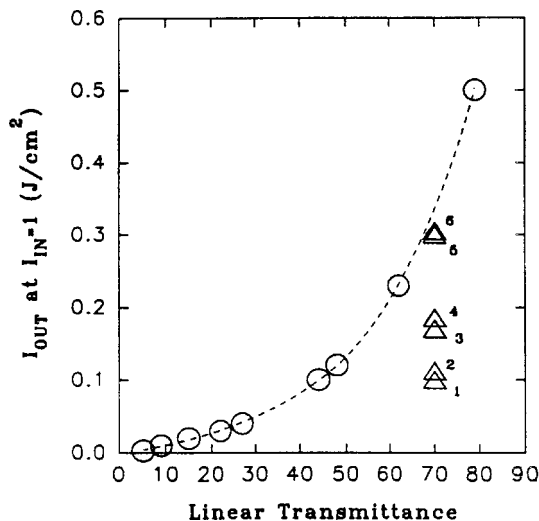


Figure 23. Optical limiting responses of the methano- C_{60} derivative **10** in toluene solutions (Δ) of different concentrations (1: 1.23×10^{-3} M, 2: 6.16×10^{-4} M, 3: 1.23×10^{-4} M, 4: 6.16×10^{-5} M, 5: 2.46×10^{-5} M, and 6: 1.23×10^{-5}) and in thick PMMA polymer films (\circ) of different linear transmittances. The output fluences at the input fluence of $1 J cm^{-2}$ are plotted as a function of the sample linear transmittance. (Reprinted with permission from [86]. © 1999 American Chemical Society.)

their limited success in such a consistent but qualitative explanation does not necessarily validate the modified model. There are still many issues to be addressed. For example, why the observed optical limiting responses of fullerenes at a high concentration can be modelled almost quantitatively [44, 61] without taking into consideration any of the contributions from bimolecular excited state processes. Further experimental and modelling efforts are definitely needed for a mechanistically more quantitative understanding of fullerene optical limiting properties.

4. Nano-materials as optical limiters

Optical limiters based on inorganic materials have been investigated from several directions. In addition to mixed metal complexes and clusters [33–41], semiconductors [1, 3, 162–172], composite materials [173–176], and recently metal and metal sulphide nanoparticles [88, 177] have been studied for their optical limiting properties.

Semiconductor materials exhibit a wide range of optical nonlinearities that have been exploited for applications in passive optical limiting. The nonlinear optical effects that are relevant to limiting laser pulses are due to the nonlinear refraction associated with the generation of free carriers and, to a lesser extent, to the absorption of the free carriers [1]. The two major classes of semiconductor optical limiters are represented by gallium arsenide and silicon. Mechanistically, materials represented by gallium arsenide and silicon are direct bandgap and indirect bandgap semiconductor optical limiters, respectively. A direct bandgap semiconductor does not induce single-photon transitions from the valence band to the conduction band, but exhibits two-photon absorption under high light intensity conditions [1]. As a result, the generation of free carriers is a two-photon absorption process. Indirect bandgap semiconductor materials rely on linear indirect absorption to generate

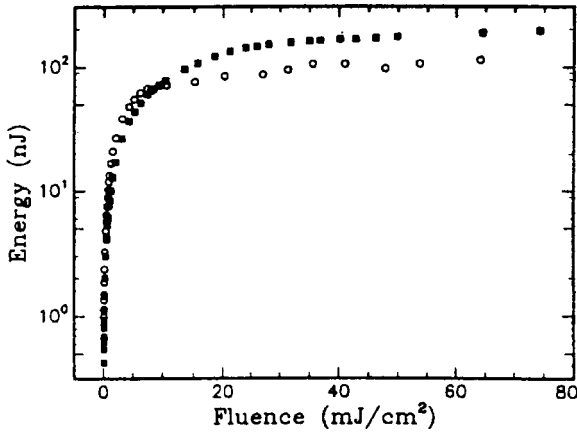


Figure 24. From [1] with the original caption (with permission from Elsevier Science). Optical limiting in Si (■) and GaAs (○) for 25 ps, 1.06 μm pulses using a $f/250$ optical system.

free carriers [1]. Despite the significant difference in free carrier generation, the underlying nonlinear optical processes in the two classes of semiconductor optical limiters are in fact quite similar.

For gallium arsenide, the nonlinear optical effects that contribute to optical limiting responses are intensity dependent rather than fluence dependent. As a result, gallium arsenide is effective only for optical limiting toward sub-nanosecond laser pulses. For example, Boggess *et al.* have shown that gallium arsenide limits picosecond pulsed laser radiation at 1.06 μm through two-photon absorption [168]. While self defocusing and optically induced melting also contribute to the observed optical limiting responses, the free carrier absorption is insignificant to the measurably optical limiting contribution [168]. Said *et al.* reported the optical limiting properties of zinc selenide in the visible spectral region [169]. Since the optical limiting in zinc selenide is based on two-photon absorption, the material is therefore effective only for sub-nanosecond laser pulses. In addition to gallium arsenide and zinc selenide, cadmium telluride and zinc telluride were investigated for optical limiting at 1.06 μm [170]. The optical limiting responses were also attributed to a two-photon absorption mechanism. Krauss and Wise measured the nonlinear absorption and refraction of cadmium sulphide, zinc sulphide, and zinc selenide using femtosecond laser pulses [171]. The use of femtosecond pulses in the investigation confirmed that the observed optical limiting responses are due to optical nonlinearities arising from two-photon absorption.

Silicon represents another class of semiconductor optical limiters. Unlike the direct bandgap semiconductor optical limiters, silicon type optical limiters are essentially fluence dependent but pulse-width independent, namely they are effective for limiting laser pulses ranging from picoseconds to a hundred nanoseconds [1]. Due to the resonant nature of the free carrier generation, however, semiconductor optical limiters represented by silicon are only effective near the bandgap (1.1 eV for silicon). Thus, the bandwidth with these limiters is rather narrow. As an example of indirect bandgap semiconductor optical limiters, gallium phosphide was studied by Rychnovsky *et al.* [172]. It was reported that the material exhibits strong optical

limiting responses toward 25 ps laser pulses at 532 nm, with the attenuation level actually close to that required for eye protection [172]. The strong optical limiting was attributed to nonlinear refraction as the dominating effect and also to free carrier absorption as a secondary mechanism [172], similar to those in the silicon optical limiters.

At nanoscopic sizes, semiconductor particles such as cadmium sulphide can be suspended in a liquid medium [178, 179]. The nanoparticle suspensions show only weak optical limiting responses toward nanosecond laser pulses [177, 179].

Recently, however, Sun *et al.* discovered that nanocrystalline silver and silver sulphide particles in polymer stabilized suspensions are excellent optical limiters [88, 177]. The nanoparticles were prepared in a newly developed method that is based on supercritical fluid technology [88, 178, 180]. In the presence of a stabilization polymer such as poly(*N*-vinyl-2-pyrrolidone) (PVP), the nanoparticles thus prepared form very stable suspensions that are in fact indistinguishable from a typical homogeneous solution. By using the stable suspensions, Sun *et al.* carried out optical limiting measurements in the same way as that for solution samples [88, 177]. Figure 25 shows the optical limiting results of silver nanocrystalline particles with an average size of 5.6 nm and a size distribution standard deviation of 0.78 nm in a PVP polymer stabilized ethanol suspension. At a linear transmittance of 90%, the nanoparticle suspension exhibits strong optical limiting responses toward 5 ns laser pulses at 532 nm, with the saturated output light fluence at the optical limiting plateau lower than those of C₆₀ in toluene solution and AlClPc in DMF solution of the same linear transmittance (figure 25) [88]. Based on the characterization experiments performed by Sun *et al.*, the optical limiting responses of the stable suspension are indeed due to nanocrystalline silver particles [88, 177].

Also shown in figure 25 for comparison are the optical limiting results of nickel metal nanoparticles in a PVP polymer protected stable suspension prepared using the same supercritical fluid method [180]. The nickel nanoparticles exhibit only marginal optical limiting responses toward 5 ns laser pulses at 532 nm, significantly different from the nanocrystalline silver particles [88]. The results seem to suggest that the excellent optical limiting properties are specific with respect to the silver nanoparticles. Such an assessment was further confirmed by a comparison of optical limiting properties of silver sulphide and other metal sulphide nanoparticles. As shown in figure 26, the silver sulphide particles with an average particle size of 7.3 nm and a size distribution standard deviation of 1.7 nm in PVP polymer stabilized ethanol suspension show strong optical limiting responses toward 5 ns laser pulses at 532 nm. The optical limiting responses of the silver sulphide nanoparticles are in fact even stronger than those of the silver nanoparticle suspension at the same linear transmittance of 90% (figures 25 and 26). However, considerably weaker optical limiting responses were observed for other metal sulphide nanoparticles including cadmium sulphide and lead sulphide in stable suspensions (figure 26) [88, 177].

Optical limiting properties of silver-containing nano-materials have also been studied under somewhat different conditions. Sahyun *et al.* [87] reported the optical limiting performance of nanosols comprising ~6 nm particles of silver bromide. The limiting was found to be on the nanosecond time scale, with low limiting thresholds in comparison with those of other optical limiting materials. The observed optical limiting responses were attributed to the formation of light absorbing cluster species upon laser excitation [87], which essentially invokes a nonlinear absorption mechanism. It was proposed [87] that the cluster species nucleate from iodide sites

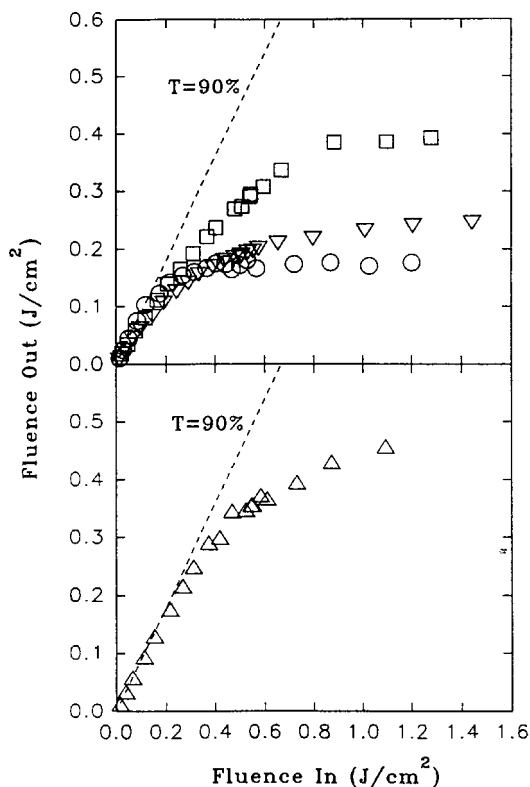


Figure 25. Optical limiting responses (5 ns laser pulses) of the nanocrystalline silver metal particles in PVP polymer stabilized ethanol suspension of 90% linear transmittance at 532 nm (○) are compared with those of C₆₀ in toluene (□), AlClPc in DMF (▽), and the nickel metal nanoparticles in DMF suspension (△) of the same linear transmittance. (Reprinted with permission from [88]. © 1999 American Chemical Society.)

in the silver bromide nanosol, which act as electron donor centres, and that the absorbance of the cluster species increases with the growth in cluster size.

Mechanistic details are not clear on the excellent optical limiting properties of silver-containing nanoparticles reported by Sun *et al.* [88]. Tentatively, a nonlinear absorption mechanism was suggested [88] on the basis of other optical spectroscopic results. It is well-documented that silver nanoparticles have interesting photoelectrochemical properties [181, 182]. Recently, Kamat and co-workers reported [183] that silver colloids of particle diameter 40 to 60 nm exhibit a strong and broad transient absorption in the visible and near-infrared wavelength region when subjected to laser-pulse excitation. The transient absorption growth monitored at 600 nm follows a single exponential kinetic equation, with a lifetime of 1.5 ± 0.1 ns [183]. The broad transient absorption was assigned to a transient state that is generated in a photoinduced intraparticle charge separation process, namely $(\text{Ag}^+ \text{e}^-)_x$. Essentially similar photoinduced redox processes were proposed to be responsible for the optical limiting characteristics of silver bromide nanosols [87]. In addition, strong nonlinear absorption at 532 nm was observed in silver sulphide–cadmium sulphide nanocomposites of ~ 10 nm in diameter [179]. The nonlinear absorption was attributed to

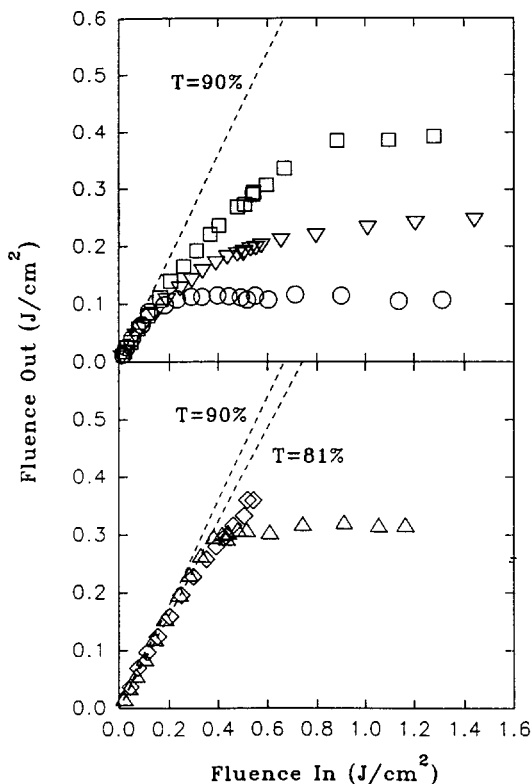


Figure 26. Optical limiting responses (5 ns laser pulses) of the silver sulphide nanoparticles in PVP polymer stabilized ethanol suspension of 90% linear transmittance at 532 nm (○) are compared with those of C₆₀ in toluene (□) and AlClPc in DMF (▽) of the same linear transmittance and also those of the cadmium sulphide nanoparticle suspension (◇) of 81% linear transmittance and the lead sulphide nanoparticle suspension (△) of 90% linear transmittance. (Reprinted with permission from [88]. © 1999 American Chemical Society.)

the free-carrier absorption that is associated with the coating of cadmium sulphide particles with silver sulphide. Similarly, Sun *et al.* suggested [88] that the strong optical limiting responses of the nanocrystalline silver metal and silver sulphide nanoparticles observed in their investigations may also be dominated by a non-linear absorption mechanism. The photoinduced electron ejection process probably produces electron holes in the nanoparticle structure, resulting in strong free-carrier type absorption on the nanosecond time scale. Speculatively, the result that the optical limiting responses of the silver metal nanoparticles are somewhat weaker than those of the silver sulphide nanoparticles (figures 25 and 26) could simply be a reflection of the difference in their ground state absorption cross-sections [88]. Because of the characteristic plasmon absorption of the silver nanoparticles, which peaks at ~ 410 nm (figure 27), the ground state absorption cross-section of the silver metal nanoparticle suspension is higher than that of the silver sulphide nanoparticle suspension [88]. Thus, the former probably has a smaller absorption cross-section ratio at 532 nm for nonlinear absorption than the latter. In this regard, since the absorption of metal sulphide nanoparticles generally blue-shifts with decreasing av-

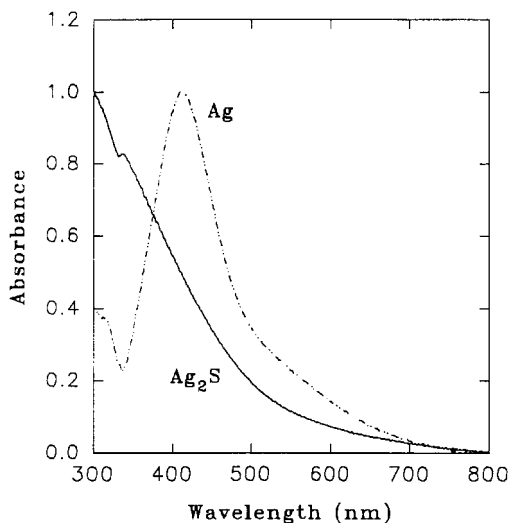


Figure 27. Absorption spectra of the silver metal and silver sulphide nanoparticles in stable ethanol suspensions at room temperature. (Reprinted with permission from [88]. © 1999 American Chemical Society.)

erage particle size, even larger absorption cross-section ratios might be obtained with silver sulphide nanoparticles of smaller average sizes, resulting in better optical limiting performance [177].

Han *et al.* used results from Z-scan measurements to show that there is enhanced nonlinear absorption when cadmium sulphide nanoparticles are coated with silver sulphide to form nanocomposites [179]. In light of the results by Sun *et al.* [88, 177], however, the enhancement explanation may require a re-examination because the perceived enhancement could be due simply to the much stronger nonlinear absorption of silver sulphide particles in the nanocomposites. It remains to be seen whether the presence of cadmium sulphide or other particles in nanocomposites with silver sulphide actually enhances nonlinear absorptive responses, perhaps through increasing the efficiency of photoinduced charge separation or the free-carrier absorption cross-section of the silver sulphide nanoparticles [177].

Since the silver-containing nanoparticles are in suspensions, possible optical limiting contributions from transient scatterings that are associated with photo-thermal processes should be considered. However, according to Sun *et al.* [88], experimental results of the nanoparticles obtained in their study do not support a predominantly nonlinear scattering mechanism established for other kinds of particle suspensions in the literature [120, 184, 185]. For suspensions of light absorbing carbon black particles, for example, the strong optical limiting responses were explained in terms of optical breakdown of absorbing carbon black particles and associated liquid solvent [120, 184, 185]. In such a mechanism, the attenuation of nanosecond laser pulses was attributed to the formation of scattering shock waves as a result of the optical breakdown. Conceptually speaking, the optical limiting mechanism for suspensions of carbon black particles is, in a broad context, similar to the nonlinear refraction mechanism that dominates the optical limiting in semiconductor materials. In both cases, the limiting of laser pulses is due to nonlinear optical effects induced by the laser irradiation.

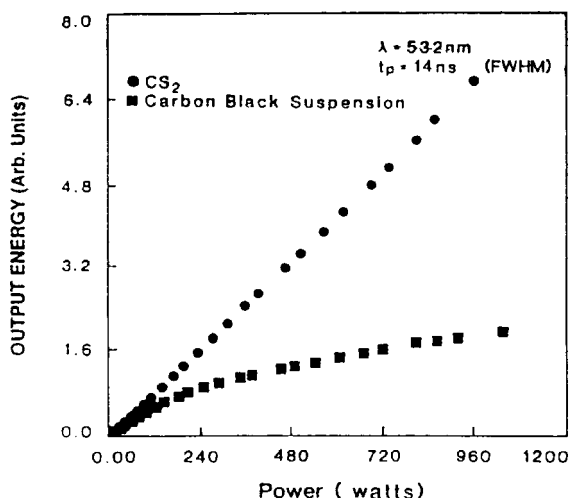


Figure 28. From [184] with the original caption, with permission from the Optical Society of America. Energy output for CS₂ and CBS as a function of input peak power for 14 ns (FWHM), 532 nm pulses focused to $\omega_0 \approx 3.5 \mu\text{m}$ for input powers of 1 to 1000 W.

Carbon black suspensions are in fact among the best optical limiters. Mansour *et al.* reported that carbon particles on the order of 35 nm are rapidly heated by the absorption of pulsed laser irradiation [184]. The light absorption leads to microplasma formation which strongly scatters the incident laser light. Higher input energies cause more heating, thus inducing further scattering that lasts up to microseconds [184]. The optical limiting in carbon black suspensions is fluence dependent rather than irradiance dependent. Because of the broad absorption over the visible wavelength region, the suspensions of carbon black particles are broadband optical limiters [184].

A significant shortcoming for the carbon black suspension optical limiters is that at high laser repetition rates the limiting performance can degrade due to the breakdown of particles and the insufficient replacement by fresh particles through diffusion into the illumination volume. According to Mansour *et al.*, carbon black suspensions are best for limiting laser pulses longer than 10 ns, but less effective for limiting picosecond laser pulses [184]. Interestingly, while the overall limiting performance is dependent on the carbon black concentration, it was found that the onset of optical limiting is essentially concentration independent. The optical limiting performance of carbon black particles is apparently affected by the particle sizes. Because longer heating times are required, higher limiting thresholds were observed for larger particles [184].

Nashold and Walter also investigated the optical limiting properties of carbon black suspensions [120, 185]. The results were discussed in the same mechanistic framework, namely that the carbon particles heat up due to laser irradiation, vaporize, and create small plasmas and shock waves to reduce the output energy by scattering and absorption. In a direct comparison of carbon black suspensions and C₆₀ solution under the same experimental conditions, the saturated output of the suspension was found to be approximately three times lower than that of the C₆₀ solution at the same 66% linear transmittance [120, 185]. Mechanistically,

however, the results suggest that the optical limiting responses of C₆₀ solution are dominated by absorption rather than scattering, whereas the responses of carbon black suspensions are due predominantly to scattering.

The results reported by Sun *et al.* [88] suggest that nanoscopic materials may represent a new frontier in the development of potent optical limiters. The optical limiting performance of the silver-containing nanoparticles is obviously among the best of all known optical limiting materials. There are many possibilities and parameters to be examined for better performing nano-material optical limiters. For example, the size distributions and surface properties of the silver-containing nanoparticles are probably important to the efficient intraparticle free-carrier generation [177]. Related effects on optical limiting performance should be examined experimentally. Systematic investigations of other classes of nano-materials for optical limiting applications are also needed. The tasks are challenging but also offer great new opportunities in the search for better optical limiters.

5. Concluding remarks

The development and application of nonlinear optical materials for limiting laser irradiation represent a relatively new but challenging research area. The optical limiters discussed here may be conceptually classified into two large categories. In one category, the materials are limiting laser irradiation through the strong absorption of electronic state(s) or species that are produced in the laser irradiation. In the other category of materials, the limiting of laser irradiation is accomplished through nonlinear optical processes or effects that are created or stimulated by the laser irradiation. Future activities in the development of optical limiters will be associated largely with the two categories. For potential breakthroughs in the development of much improved optical limiters, the supramolecular reverse saturable absorption concept offers great opportunities. Finally, greater efforts centred on the use of optical limiting materials in optimized limiter devices for practical applications are expected.

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