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Phthalocyanines and related compounds: organic targets for nonlinear optical applications

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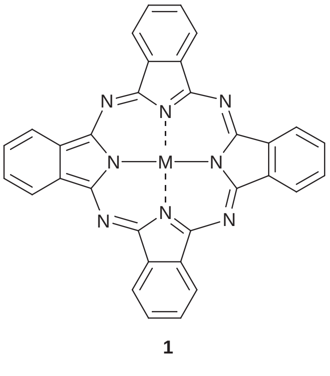
Phthalocyanines (Pcs) and related compounds with their extended two-dimensional π-electronic delocalization are important targets to study nonlinear optical responses. The tailorability of these macrocycles allows the fine-tuning of the chemical structure and nonlinear optical response. In this article, the design and main properties of phthalocyanines for second- and third-order nonlinear optical (NLO) and optical limiting applications are discussed, both at the microscopic and macroscopic level. The points of view of synthetic organic chemists and physicists are accorded, the main aim of the review being to highlight the key problems of the field and place them within the general context of NLO materials.

Phthalocyanines[1,2] (Pcs) **1** are a family of aromatic macrocycles based on an extensive delocalized two-dimensional 18π-electron system which exhibit a large number of unique properties. They are highly stable and versatile compounds, capable of including more than 70 different metallic and non-metallic ions in the ring cavity. Moreover, it is possible to incorporate a variety of peripheral substituents around the phthalocyanine core, as well as replace some of the four isoindole units by other heterocyclic moieties, giving rise to different phthalocyanine analogues. Phthalocyanines also show remarkable optical properties. The linear optical spectra of these compounds are dominated by two intense bands, the Q band (centered at around 670 nm) and the B band in the near UV region (at around 340 nm), both correlated to π–π* transitions (Fig. 1). Another peculiar and useful feature of these compounds is their ability to form different kinds of condensed phases, such as discotic liquid crystals,[3,4] when they are adequately functionalized with long lipophilic chains. Furthermore, it is possible to build thin films by several techniques, such as spin-coating,[5] molecular beam epitaxy (MBE)[6] and Langmuir–Blodgett (LB) technology,[5] that allow the fabrication of devices. Notably, phthalocyanine-based thin films have been applied to a wide range of technological areas: gas sensors,[7,8] electrochromic devices,[9] field effect transistors[10] and photovoltaic cells.[11]



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Following the discovery of the laser by Maiman[12] in 1960, considerable research attention has been paid to the field of nonlinear optics[13,14] in order to develop opto-electronic technologies,[15,16] such as high-speed information processing and optical communications. In the early stages, research work was focused on inorganic materials but, in the last 20 years, interest in organic materials for nonlinear optical applications has markedly increased.[13,14,17–19] They offer several advantages over inorganic materials, such as large nonlinearities, ultrafast response times and easy and economic processability, for the preparation of films and miniature integrated optics devices. Moreover, it is possible to optimize their NLO properties by rational modification of their structure.

Nonlinear processes can be broadly classified in two main categories, *parametric* and *non-parametric*. Macroscopic *parametric* processes are described through the following expansion of the light-induced polarization in powers of the wave electric field [eqn. (1)],

$$P = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \ldots \qquad (1)$$

where $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are, respectively, the linear, first-order and second-order susceptibilities. At the microscopic level a similar expansion can be written for the molecular polarization [eqn. (2)],

$$p = \alpha E + \beta EE + \gamma EEE + \ldots \qquad (2)$$

α, β and γ being the linear polarizability and the quadratic and cubic hyperpolarizabilities, respectively. The higher-order terms in eqn. (1) and (2) are not relevant in most experiments. Away from resonances, *parametric* processes may become

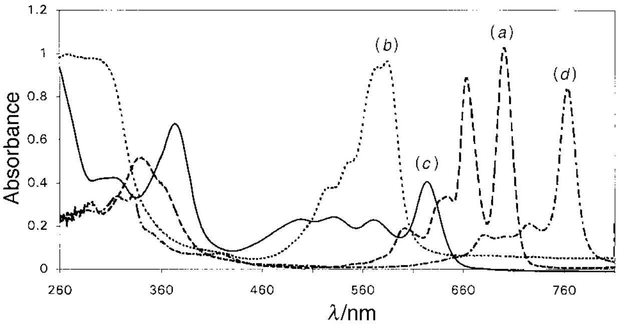


Fig. 1 UV–VIS spectra of (*a*) tetra(*tert*-butyl)phthalocyanine (5×10^{-6} M), (*b*) trinitrosubphthalocyanine **10c** (1.9×10^{-5} M, (*c*) triazolephthalocyanine **9** ($R^1 = R^2 = H$, $R^3 = Bu^t$, $M = Ni$) (2.1×10^{-5} M) and (*d*) nickel tetra(*tert*-butyl)naphthalocyanine (8.5×10^{-5} M)

extremely fast (*i.e.* subpicosecond response times), and obey very selective phase-matching conditions.

On the other hand, *non-parametric* processes are always resonant and rely on light-induced changes in the population of the energy levels of the system (*optical pumping* nonlinearities). Susceptibilities (hyperpolarizabilities) cannot be properly defined and phase-matching conditions are not applicable. They are generally much slower and the response time depends on the lifetimes of the involved transitions. This article mostly focuses on parametric processes, both second- and third-order, whereas the non-parametric processes will be considered in a final section dealing with the subject of optical limiting.

Organic materials for nonlinear optics are typically based on a highly polarizable π-conjugated system. Phthalocyanines and related compounds, with their extended two-dimensional π-electron delocalization, are key targets to study nonlinear optical processes[14,20] and are very promising candidates for optical switching and optical limiting devices. The tailorability of phthalocyanines allows the fine tuning of the chemical structure and nonlinear optical response. In this way, the introduction of adequate peripheral substituents can alter the electronic structure of the molecule and originate effective intramolecular charge transfer processes. Additionally, the possibility of introducing different central metal atoms provides architectural flexibility to optimize the NLO and other physical properties. It is also possible to modulate the nonlinear response by conventional organic synthesis, varying the extension of π-electron delocalization (*i.e.* the naphthalocyanine system) or modifying the electronic structure through formal substitution of one or more isoindole units by other heterocyclic moieties. On the other hand, phthalocyanines present high self-organizing abilities, mainly due to the strong π–π interactions between their aromatic rings. The possibility of self-assembling two or more phthalocyanine units in one- or even two-dimensional architectures can promote NLO properties at the supramolecular level by electron delocalization.

In this article we will discuss second- and third-order parametric NLO properties of phthalocyanine-related compounds and materials, both at the microscopic (molecular) and macroscopic level. The connection between the two views will be emphasized. Finally, due to the present relevance of optical limiting devices we will also discuss this (mostly non-parametric) type of NLO response, involving changes in the populations of the energy levels of the system. Since some useful and detailed reviews on the subject have been published in recent years, we will focus our discussion on the latest results. Moreover, we will put the accent on the basic problems and general trends of the field rather than on an exhaustive description of data. The main aim should be to highlight the key problems and place them within the general context of NLO materials.

Second-order NLO properties of phthalocyanines and analogues

There has been continuous interest in the search for materials exhibiting large macroscopic second-order nonlinearities[21] because of their applicability in frequency doubling, parametric oscillation and high-speed light modulation.[16] Most experiments yield $\chi^{(2)}$ (2ω: ω, ω) through second-harmonic generation (SHG) techniques and $\chi^{(2)}$ (ω: ω, 0) by using electrooptic methods. It has been assessed that the second-order optical nonlinearity in many organic compounds arises from a highly polarizable π-conjugated system capped with groups of different electron affinities. To date, the research effort has mostly focused on one-dimensional molecules, *i.e.* donor–acceptor disubstituted polyenes,[22] which present one dominant hyperpolarizability component lying in the direction of the intramolecular charge transfer (ICT) axis. For these organic molecules, the experimental determination of the hyperpolarizability is usually carried out using the traditional EFISH[23,24] (electric field induced second harmonic generation) measurements in solution. In these experiments, a strong electric field applied to the sample gives rise to the loss of inversion symmetry and allows second-harmonic generation to occur. Recently, a new technique based on hyper-Rayleigh light scattering (HRS)[25–27] has been developed. It uses an intense laser beam that is focused on an isotropic solution of the nonlinear chromophores. The scattered frequency-doubled light intensity arises from fluctuations of the induced molecular dipoles and is proportional to the square of the incident fundamental intensity. One advantage of this technique over EFISH is that it can be applied to both polar and nonpolar molecules.

Due to their extensive delocalized two-dimensional π-system and their centrosymmetric structure, non-substituted or symmetrically substituted phthalocyanines have been commonly studied as third-order NLO materials. However, an intriguing topic is the observation of appreciable SHG from thin films of centrosymmetric phthalocyanines,[28–33] such as unsubstituted Co^{II}, Cu^{II}, Zn^{II} and metal-free derivatives. Several explanations have been advanced such as excited-state noncentrosymmetric relaxation of Cu ions, surface effects and magnetic dipole and electrical quadrupole contributions. These latter nonlocal effects are ignored in the usual local description of NLO responses in terms of polarizabilities and susceptibilities. Recently, the quadrupole origin of the second-order nonlinearity appears to be supported by careful measurements on MBE films.[32] SHG of electric quadrupole origin has been also observed[34] in isotropic and discotic phases of a thiooctadecyl-substituted phthalocyanine. Resonant states due to inter- and intra-molecular transitions have been suggested.

The SHG response has also been observed from nickel(II) tetrakis(cumylphenoxy)phthalocyanine.[35] In this case, random placement of the peripheral groups makes this material non-centrosymmetric, despite having the same kind of substitution in all four isoindole moieties. On the other hand, SHG has been observed in films of unsusbstituted vanadyl phthalocyanine.[36,37] This molecule is non-centrosymmetric and polar, since the V=O moiety lies perpendicular to the macrocycle plane. As expected, the second harmonic intensity increased quadratically with film thickness.

It has been suggested[38] that unsymmetrically substituted phthalocyanines with suitable donor and acceptor groups capable of displaying efficient intramolecular charge transfer should exhibit second-order NLO responses. For this reason, some research work has been carried out in order to develop non-centrosymmetric peripherally substituted phthalocyanines. On the other hand, some molecular engineering approaches to break the inversion symmetry of the macrocycle itself have been also elaborated. These two strategies will be considered successively in the next sections.

Unsymmetrically substituted phthalocyanines

The synthesis of phthalocyanines[1,2] involves a cyclotetramerization reaction of a phthalonitrile or 1,3-diiminoisoindoline. When the condensation is carried out between identically substituted precursors, centrosymmetrical compounds or mixtures of regioisomers are obtained. The preparation of phthalocyanines with different substituents on the isoindole units requires the synthetic strategies described below.

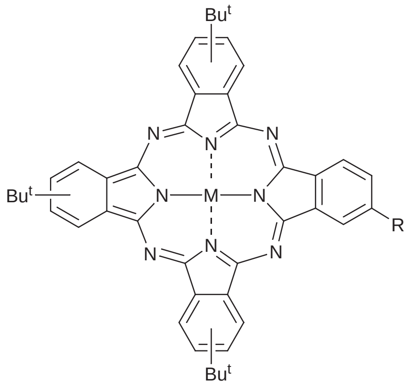
(i) Attachment of a substituted diiminoisoindoline to an insoluble polymer[39] and subsequent reaction with an excess of another differently substituted diiminoisoindoline, followed by the liberation of the phthalocyanine from the polymer.

(ii) Cross-condensation of a diiminoisoindoline derivative with a 1,3,3-trichloroisoindolenine or with another sterically crowded iminoisoindoline.[40] In this way, identically face-to-face substituted phthalocyanines are obtained.

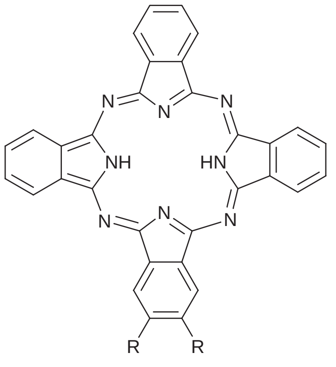
(iii) Ring-expansion of a three-unit macrocycle (subphthalocyanine, see below) with a substituted diiminoisoindoline.[41]

(iv) The most usual method is the statistical condensation of two differently substituted dinitriles or diiminoisoindolines followed by chromatographic separation of the statistical mixture of compounds.[42] Commonly, 3:1 to 9:1 ratios are employed, which favor the formation of the unsymmetrically substituted phthalocyanine with three identically substituted isoindole subunits.

Probably due to the difficulty in the preparation of pure unsymmetrically substituted phthalocyanines, few reports on the second-order NLO properties of this kind of compound have been published. Wada, Sasabe and Liu and co-workers reported SHG experiments on both Z-type deposition and in alternating deposition LB films of metal-free[43,44] and copper[45] nitrotri(*tert*-butyl)phthalocyanine (**2a** and **2b**, respectively). The second-order NLO response of the film was found to be fairly intense ($\chi^{(2)}=2\times10^{-8}$ esu for **2a** and $\chi^{(2)}=2\times10^{-5}$ esu for **2b**), especially in the case of the copper compound. In the case of alternated films, the dependence of the second harmonic intensity on the number of bilayers is nearly quadratic. Some experiments have also been carried out on LB films of metal-free aminotri(*tert*-butyl)phthalocyanine **2c**,[46] showing a similar SHG response to that of the related metal-free phthalocyanine **2a**.



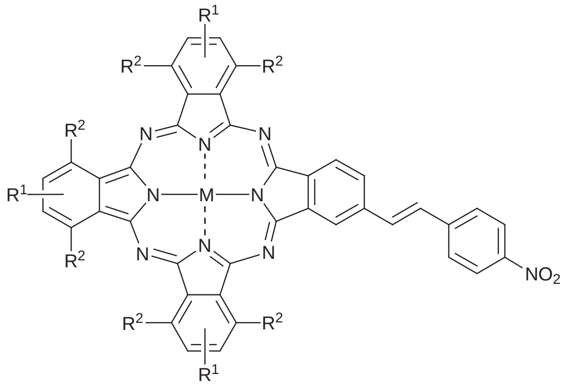
2a R = NO_2; M = 2H
2b R = NO_2; M = Cu
2c R = NH_2; M = 2H
2d R = $SO_2C_6H_4CH_3$; M = 2H



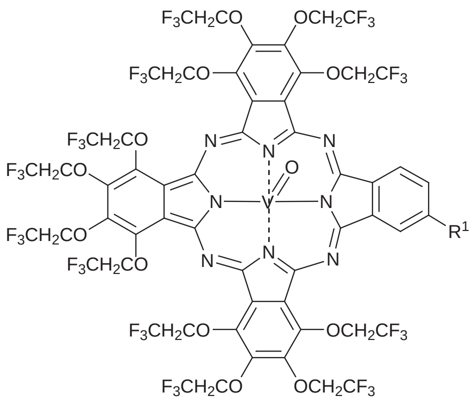
3a R = Bu^t
3b R = OC_8H_{17}

The first studies of the microscopic nonlinear responses of unsymmetrically substituted metal-free phthalocyanines, such as **2a**, **2d**, **3a** and **3b**, have been recently accomplished by third-harmonic generation (THG) and EFISH generation techniques, at 1340 and 1064 nm, respectively.[47,48] These experiments do not reveal evidence of important first-order hyperpolarizability. This fact suggests that the vector part of β is not important, the main contribution to the EFISH signal arising from the electronic contribution to the overall cubic hyperpolarizability ($\gamma_{\mathrm{EFISH}}=-12\times10^{-34}$; $\gamma_{\mathrm{THG}}=-19\times10^{-34}$ for compound **2d**). However, a significant influence of intramolecular charge transfer on the cubic nonlinear response (γ) has been evidenced and correlated to the relative strengths of donor and acceptor substituents.[48] This correlation appears to be related to a strong two-photon resonance enhancement of the ICT contribution to γ. This enhancement effect of the γ_{THG} values due to the high dipolar moment associated to strong donor and acceptor substituents follows the trend previously observed in some porphyrin and phthalocyanine systems.[49,50]

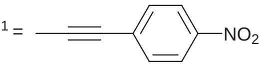
A synthetic strategy that has been pursued in order to enhance the quadratic hyperpolarizabilities is the extension of the conjugation length between the donor and acceptor groups, by introducing π-delocalized electron-acceptor substituents.[51] This approach seems quite reasonable, considering theoretical[38,52] predictions and experimental[53,54] results on the relationship between the magnitude of the first hyperpolarizability and the extent of the π-electron conjugation previously found for other systems. The influence of the position and electronic character of the substituents and the role of the central metal on the second and third NLO responses of this kind of systems, such as **4a**–**e**, has been studied.[55] EFISH experiments at 1900 nm do not show evidence of significant first-order hyperpolarizability and the main contribution to the EFISH signal derives from the third order electronic contribution to γ (2ω: ω, ω, 0). But in this case, γ_{EFISH} and γ_{THG} are one order of magnitude larger than those of unsymmetrically substituted phthalocyanines **2a**, **2d**, **3a** and **3b**, thus demonstrating the efficacy of the π-electronic extension in enhancing the nonlinear response (see next section).



4a R^1 = Bu^t, R^2 = H,M = Cu
4b R^1 = Bu^t, R^2 = H, M = Co
4c R^1 = Bu^t, R^2 = H, M = Ni
4d R^1 = H, R^2 = C_8H_{17}, M = Ni
4e R^1 = H, R^2 = OC_8H_{17}, M = Ni

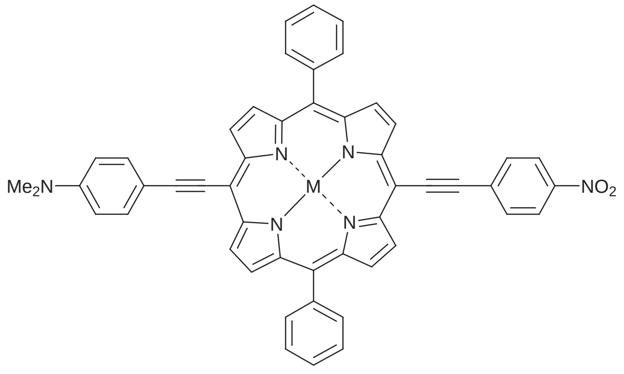


5a R^1 = NO_2

5b R^1 =


Other different 'push-pull' phthalocyanines (**5a**, **b**), some of them with exocyclic extended conjugation (**5b**), have been also prepared.[56–58] These compounds bear donor groups that suppress molecular agreggation, even in the solid state. SHG experiments were carried out on spin-coated poly(methyl methacrylate) (PMMA) films doped with unsymmetrical vanadyl phthalocyanines **5a** and **5b**.[57,58] The authors reported that films of **5b** showed larger second-harmonic signals than those of **5a**, thus pointing out the effect of the extended π-conjugation.

Similar relationships between the nonlinear response and the π conjugation length between the donor and acceptor end groups have been established for porphyrin systems.[49,59–61] Appropiate tuning of the π-delocalized cyclic porphyrin structures may also result in large second harmonic responses. EFISH measurements of unsymmetrically substituted aminonitrotetraphenyl porphyrins reported by Suslick *et al.*[49] showed first hyperpolarizability values that were moderately high $[(10\text{–}30)\times10^{-30}$ esu]. Similar values have been found in related compounds.[59] HRS experiments carried out on porphyrins with extended π-conjugation (**6**), achieved by the introduction of arylethynyl groups, showed larger β values than those of their less-conjugated counterparts.[60] More recently, SHG coefficients of a number of 'push-pull' porphyrins with extended π-conjugation have been analyzed using semiempirical methods.[61]



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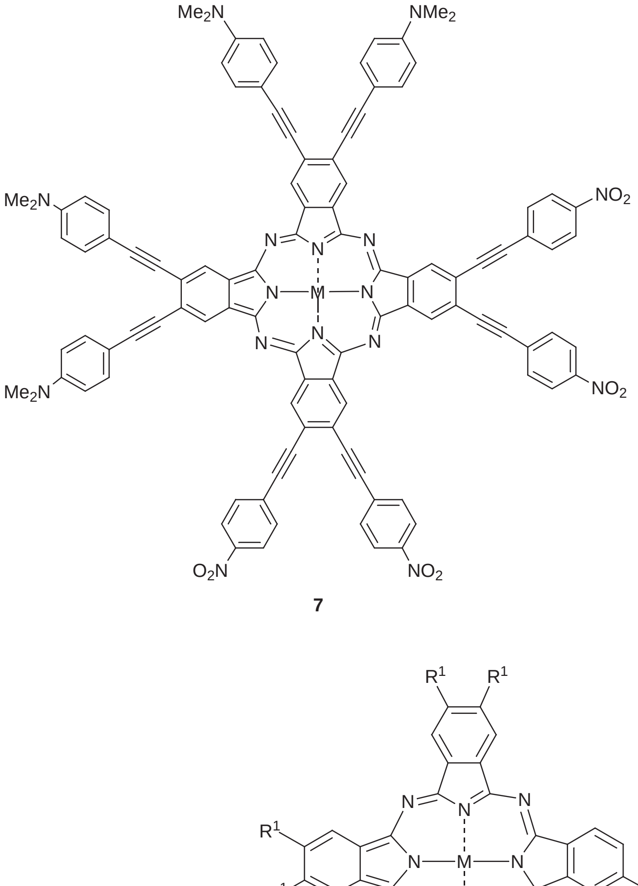

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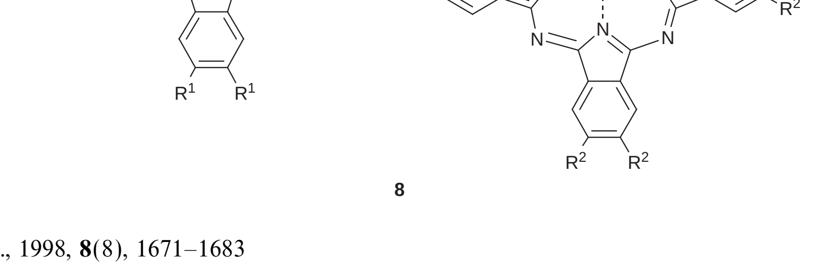
The results obtained in some arylethynyl-substituted porphyrins, mentioned above, suggest that related phthalocyanine structures such as **7** are promising candidates for displaying large first order hyperpolarizabilities.[62] Moreover, theoretical calculations on porphyrins[60] suggest that it should be possible to obtain larger *β* values in structures based on two differently substituted phthalocyanine units linked by an ethynyl bridge, such as **8**.[63]

Unsymmetric phthalocyanine-related systems

Triazolephthalocyanines (TPcs)[64] **9** are core-modified phthalocyanines resulting from a formal substitution of one isoindole unit by a 1,2,4-triazole moiety. These compounds represent a novel class of intrinsically unsymmetric 18π-electron aromatic metallomacrocycles. Triazolephthalocyanines have a peculiar optical spectrum, which is shown in Fig. 1, showing absorption maxima shifted to lower wavelengths in comparison to those of phthalocyanines. Synthesis of triazolephthalocyanines involves either a one-step metal(II) template-assisted condensation of 3,5-diamino-1,2,4-triazole and the corresponding 1,3-diiminoisoindoline[64] or a stepwise approach.[65] The latter allows the introduction of both electron-donor and -acceptor substituents, able to promote charge-transfer processes. Actually, the acceptor character of the triazole subunit gives rise to a strong dipolar moment, which could be increased by the introduction of donor groups in the isoindole moiety opposite to the triazole one.

Another remarkable feature of these compounds is their ability to self-organize in thin films *via* the Langmuir–Blodgett technique.[66] The amphiphilic structure and the possibility of introducing long-chain substituents on the isoindole units make them suitable for preparing in-plane oriented LB films. Studies on the second- and third-order NLO properties in solution of these novel and promising class of compounds are currently being performed.[67]



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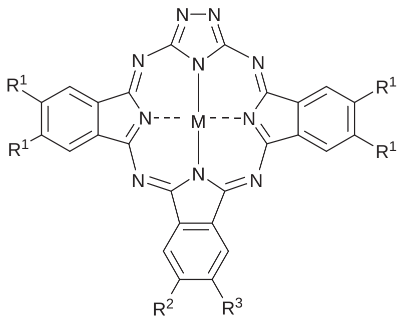

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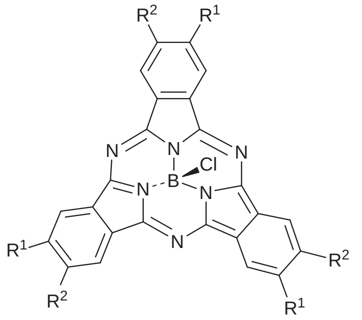


10a $R^1 = R^2 = H$
10b $R^1 = H, R^2 = Bu^t$
10c $R^1 = H, R^2 = NO_2$
10d $R^1 = H, R^2 = I$
10e $R^1 = H, R^2 = SO_2C_8H_{17}$
10f $R^1 = H, R^2 = SC_8H_{17}$
10g $R^1 = R^2 = SO_2C_8H_{17}$
10h $R^1 = R^2 = SC_8H_{17}$
10i $R^1 = H, R^2 = C{\equiv}C{-}C_6H_4NO_2$

On the other hand, formal structural modifications of the phthalocyanine ring allow the reduction of its symmetry, yielding intrinsically non-centrosymmetric compounds like subphthalocyanines (SubPcs).[68,69] They are cone-shaped 14π-electron aromatic compounds, having three coupled isoindole units which contain a boron atom in the center with an axial halogen atom. The molecular symmetry can be C_1, C_3 or C_{3v}, depending on the number and position of the substituents. Preparation of SubPcs is carried out by a condensation reaction of phthalonitrile in the presence of BCl_3 or BBr_3. The optical spectrum of a subphthalocyanine displays the same two bands as Pcs but slightly shifted to the blue (Fig. 1).

In the early nineties, Ledoux and Zyss brought into consideration octupolar molecules for second-order nonlinear optics.[70] These molecules lacking a permanent dipole moment can exhibit non-zero β due to the octupolar contribution. Both dipolar and octupolar contributions to the hyperpolarizability have to be considered in accordance with the decomposition $\beta = \beta_{j=1} \oplus \beta_{j=3}$, valid whenever Kleinman's symmetry applies. The adequate linear combination of the cartesian components β_{ijk} of the β tensor generates irreducible representation $\beta_{j=1}$ (with dimension 3) and $\beta_{j=3}$ (with dimension 7) of the rotation group. Up to now, most of the attention has focused on the dipolar part, $\beta_{j=1}$, of β. Nevertheless, much research work has been centered recently on octupolar systems,[71] mainly due to some advantages they may present over dipolar ones, including non-centrosymmetric crystallization and improved efficiency-transparency trade-off. The development of the HRS technique enabled experimental determination of the hyperpolarizability of these octupolar molecules.

Thus, some recent experiments with subphthalocyanines have pointed out the possibility that these compounds may behave as predominantly octupolar. Preliminary HRS experiments on unsubstituted (**10a**) as well as tri-*tert*-butyl- (**10b**) and trinitro-substituted (**10c**) SubPcs evidenced high average $\langle \beta^2 \rangle$ values,[72] especially in the case of compound **10c**. On the other hand, the electric field-induced second-harmonic generation yield from the same molecules was found to be very low. This result suggested that the measured β should be mostly associated to the octupolar component, arising from the cone-shaped trigonal geometry. More recently, these results have been revised and completed.[73] A systematic study of the microscopic NLO response of differently tri- and hexa-substituted subphthalocyanines, such as **10b**–**i**, has been accomplished in order to elucidate the role of donor and acceptor substituents. EFISH experiments revealed that acceptor groups induce a much larger β than donor groups, which may be associated with a correspondingly larger dipole moment for the excited state. The β_{HRS} values are also strongly dependent on the donor/acceptor character of the substituents and show the same trend as the previously mentioned β values.

Subphthalocyanines present a moderate permanent dipole moment which is presumably aligned along the B—Cl axis for symmetry reasons. The existence of a dipole moment offers the additional advantage of molecular ordering in spin-coated films *via* corona-poling. In fact, the second-order susceptibilities of both evaporated ($\chi_{31}{}^{(2)} = 2.36 \times 10^{-9}$ esu) and spin-coated films ($\chi_{31}{}^{(2)} = 9.62 \times 10^{10}$ to 1.14×10^{-9} esu) of trinitro-substituted subphthalocyanine **10c** have been determined *via* SHG experiments.[74] The high SHG yield also obtained for evaporated samples suggests that a strong ordering is achieved during the deposition process. Detailed studies of the SHG in trinitro- (**10c**), triiodo- (**10d**) and trioctylsulfonyl-subphthalocyanine (**10e**)[75] thin films have more recently been carried out. They have allowed the determination of the three non-zero elements of the $\chi^{(2)}{}_{ij}$ tensor in the film reference frame. The $\chi^{(2)}{}_{31}$ component is the highest, at variance with the case of linear (one-dimensional) molecules for which the relation $\chi^{(2)}{}_{33} = 3 \times \chi^{(2)}{}_{31}$ is expected. Assuming thermal equilibrium under the poling field, the components of the β tensor referred to the molecular axes have been also evaluated. The value for the axial component β_{33} is very close to zero.

Third-order NLO response of phthalocyanines and related compounds

There is a larger variety of third-order parametric effects in comparison to those related to second-order. They are described by $\chi^{(3)}(\omega : \omega_1, \omega_2, \omega_3)$ susceptibilities having different frequency dependencies or dispersion factors.[76] Also some different physical mechanisms may contribute to the various processes. For example, third-harmonic generation (THG) only involves electronic mechanisms, whereas nonlinear refraction may result from electronic as well as thermal and optical pumping mechanisms. At the molecular level, design criteria for optimized response are not as well-established as for second-order effects, although extensive electron conjugation appears indispensable. A similar situation applies to the macroscopic level and the role of molecular organization and packing has not been clearly ascertained yet.

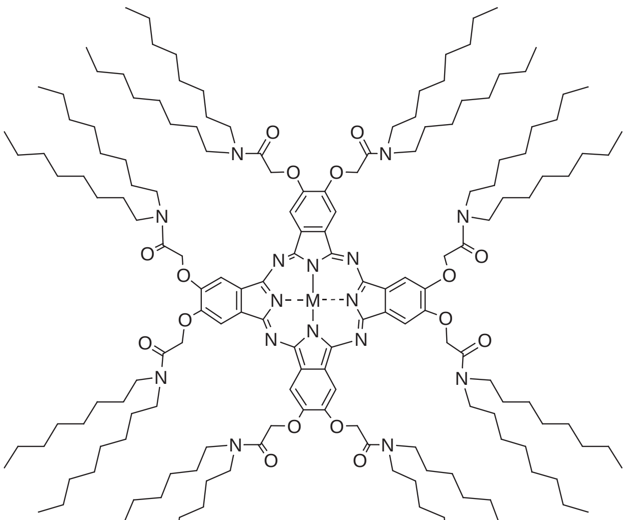
A number of experimental techniques are available to learn about third-order NLO processes and measure the corresponding susceptibilities. Most works use one of these methods: THG,[77] degenerate four-way wave mixing (DFWM)[78] and Z-scan.[79] Since they measure different susceptibilities, the comparison of the results is not always easy and depends on the experimental parameters (excitation wavelengths, pulse lengths). THG measures $\chi^{(3)}$ $(3\omega : \omega, \omega, \omega)$ and exclusively involves electronic processes. On the other hand, DFWM measures $\chi^{(3)}$ $(\omega : \omega, -\omega, \omega)$ and may include other contributions (thermal, non-parametric, *etc.*) whose relative importance depends on experimental conditions. A similar situation applies to Z-scan, which measures nonlinear refraction and absorption and may also respond to several mechanisms. In these latter two techniques, ultrafast pulse experiments are necessary for a meaningful comparison with the THG results. The third-order NLO response at microscopic and macroscopic level found in phthalocyanine derivatives will be discussed in the next sections.

Molecular hyperpolarizabilities

The optimization of the second-order molecular hyperpolarizabilities is an essential requirement for the design of useful materials for third-order NLO applications. Hence, it is interesting to clarify the factors affecting microscopic third-order optical nonlinearity in phthalocyanines, such as peripheral substitution, role of the central ion, aggregation of the metallomacrocycles, and so on.

Molecular hyperpolarizabilities $\gamma\ (\omega:\omega, -\omega, \omega)$ and $\gamma\ (3\omega:\omega, \omega, \omega)$ for a large number of metallophthalocyanines in solution have been determined by means of DFWM and THG experiments, respectively, and the results summarized in previous reviews.[14,20]

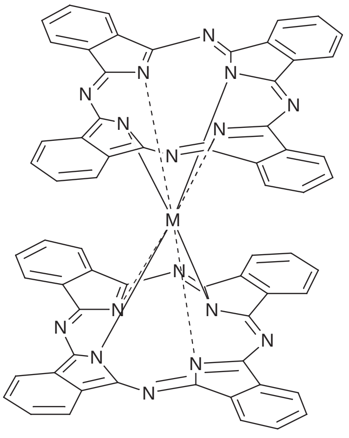
Experimental determination of both the amplitude and phase of the hyperpolarizability of compounds **11a**–**d**, has been recently achieved by THG and EFISH experiments.[80,81] The data on the phase are essential for a reliable analysis of the experiments. The real and imaginary parts of γ have been obtained from the concentration dependence of the harmonic intensity. Data for the free phthalocyanines have been satisfactorily explained in terms of a four-level model including two one-photon allowed levels (corresponding to the Q and B bands) and a two-photon allowed level placed at around 500 nm from the ground state. Independent evidence for the two-photon level has also been gathered from nonlinear absorption experiments on films.[82]



11a M = 2H
11b M = Cu
11c M = Ni
11d M = Co

The role of the central metal ion on the NLO response is a problem of physical relevance and it has been addressed in a number of studies using both solutions as well as thin films[80,83–85] (see also below). Although the situation is not yet completely clear, marked progress has recently been achieved. A clear enhancement of the cubic hyperpolarizability has, indeed, been observed for metallophthalocyanines containing uncomplete d-shell transition ions, particularly cobalt.[80] However, the enhancement is critically dependent on the excitation wavelength, suggesting the importance of frequency dispersion effects. In fact, large resonance enhancements have been observed for (electronic) EFISH at 1064 nm and have been associated with one-photon resonance with a d–d transition occurring at about 1000 nm. Similar or even larger effects have been also observed in DFWM experiments where resonance at the same wavelength is occurring.[83,84] On the other hand, THG experiments at 1346 nm do not show significant enhancement, possibly due to the dominance of a strong resonance at 3ω with the B band.[80]

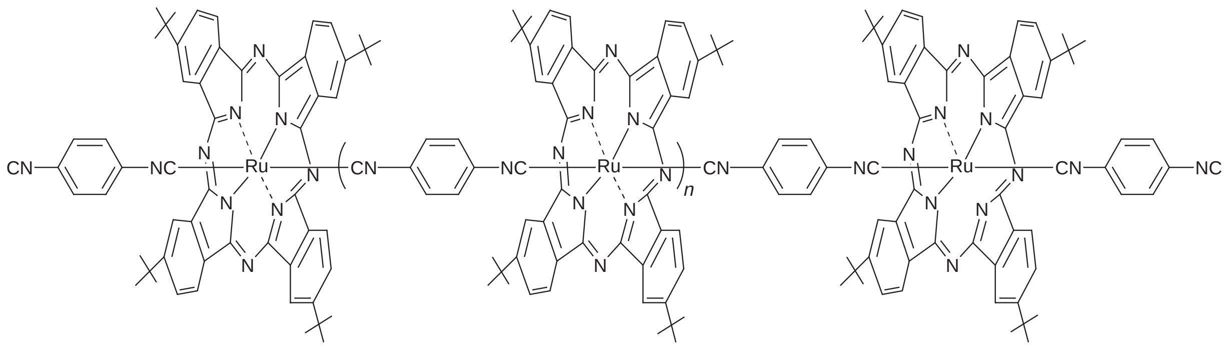
The effect of transition and rare-earth metals (M = Sc, Lu, Yb, Y, Gd, Eu, Nd) on γ has also been investigated in bis(phthalocyanines) **12**.[86] The γ values were large, as expected for such highly delocalized systems. The differences found in this series of compounds seem to be exclusively due to resonance effects.



12 M = Sc, Lu, Yb, Y, Gd, Eu, Nd

It is well-known that the introduction of peripheral substituents can modify the third-order NLO response by altering the electronic structure of phthalocyanines. The NLO characterization of a family of unsymmetrically donor- and acceptor-substituted metallophthalocyanines (MPcs), such as **2a**, **2d**, **3a** and **3b**, has been made by EFISH and THG at 1064 and 1340 nm, as mentioned above. A clear correlation of the γ hyperpolarizability with the Hammett parameter for the compounds has been obtained,[48] so that γ becomes maximal for high absolute values of the parameter, *i.e.* for molecules having either strong donor or acceptor groups. A simple analysis based in a two-level model for the Q-band transition provides a rationale to account for the observed trends.

The influence of molecular stacking on the microscopic NLO response has not yet been sufficiently investigated. However, some theoretical analyses have identified two mechanisms which lead to enhancements in the value of $\gamma\ (-\omega:\omega, -\omega, \omega)$ for cofacial covalently linked phthalocyanine dimers and trimers over that of the monomers.[87] This analysis is in agreement with recent DFWM experiments which showed a strong enhancement of $\gamma\ (-\omega:\omega, -\omega, \omega)$ for PcSiO oligomers as a function of the number of macrocycles.[88] In this case π–π overlapping between the phthalocyanine macrocycles takes place. Thus, a 24-fold increase on going from monomers to dimers and 4-fold from dimers to trimers has been measured. However, THG experiments at 1064 nm of spin-cast films of $[\mathrm{Bu^t}_4\mathrm{PcRu(dib)}]_n$ oligomers **13** (dib = 1,4-diisocyanobenzene) revealed that the NLO response is mainly determined by the individual phthalocyanine units. In this case, compared with the previous PcSiO oligomers, longer interplanar distances between two adjacent macrocycles, originated by the diisocyanobenzene bridging ligands, prevent the π–π overlaping and, therefore, the achievement of one-dimensional supramolecular optical behaviour.[89]



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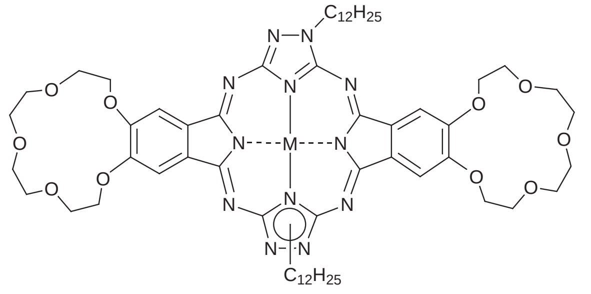
Third-order experiments at the molecular level have also been performed on Pc-related compounds, such as porphyrins and metallotriazolehemiporphyrazines. The non-resonant cubic hyperpolarizabilities of several tetraphenylporphyrin-substituted derivatives have been measured by Z-scan at 748 nm.[90] Data are discussed in terms of the interaction between the porphyrin core and the external substituents. Moreover, the third-order nonlinear susceptibility of porphyrin oligomers has been also investigated by Z-scan with 30 ps laser pulses at 640 and 1064 nm.[91] The real part has been found to be proportional to the number of monomer units. The case of metallotriazolehemiporphyrazines **14** is also interesting since a low-lying two-photon allowed level, in addition to two one-photon allowed ones, are required to account for both the real and imaginary components of the hyperpolarizability.[92] An influence of unfilled d-shell metal substitution has also been measured in this kind of compound and attributed to d–d forbidden transitions, as in phthalocyanines.[93]



14 M = 2H
M = Mn
M = Cu
M = Co
M = Fe
M = Pb
M = Zn

One should also mention that efforts have been made to theoretically understand the third-order NLO behavior of porphyrins and phthalocyanines, as derived from their electronic structure.[94]

Thin films

The processability of phthalocyanines in different types of thin films allows the study of the macroscopic NLO responses. A variety of methods for deposition of Pc films have been used. Since the structure is different depending on the particular method and it is not often well-characterized, detailed quantitative comparison is not easy, although some general trends have been clearly identified. In many cases the behaviour measured in films is consistent with that found at the molecular level. As a general rule, NLO studies in films should be combined and correlated with other structural characterization methods in order to achieve meaningful conclusions.

Films produced by sublimation and laser ablation. Due to the high thermal stability of Pcs, films of these compounds have been prepared by sublimation and their NLO properties have been investigated by a number of researchers.[14,20] More recent work has focused on the spectral dependence of the susceptibilities. The dispersive behavior of the magnitude and phase of $\chi^{(3)}$ $(3\omega:\omega, \omega, \omega)$ for evaporated metal-free and copper Pc films have been studied[95] *via* third-harmonic generation spectroscopy in the range from 950 to 2000 nm. A two-photon state lying at about 500 nm has been identified in both Pcs, confirming the model proposed[80] to account for γ $(3\omega:\omega, \omega, \omega)$ data in solution. Moreover, for the Cu-Pc an additional two-photon state located at about 1000 nm has been inferred from the spectra, also in accordance with the solution results. Anyhow, the microscopic structure of the films should be very relevant in determining the NLO response. In fact, it has been shown that the microcrystal size and orientation in vacuum-deposited SnPcs on a rubbed polymide surface strongly affect the THG susceptibility.[96]

NLO susceptibilities of vacuum-deposited Pc-related compounds, such as naphthalocyanines,[97] have also been investigated. In particular, THG experiments have been performed in films of subphthalocyanine derivatives lacking inversion symmetry.[98] The spectral dependence for the amplitude and phase of $\chi^{(3)}$ have been investigated in the range 959 to 2000 nm. $\chi^{(3)}$ values are about three times higher than those of phthalocyanines. A four-level model including the ground state and three one-photon excited states (B, Q and a shoulder at 540 nm) satisfactorily fits the data.

Finally, one should mention that laser ablation methods have also been used recently as an alternative to thermal sublimation.[99]

Spin-coated films. Spin-coating is a simple technique that produces locally-homogeneous, good quality films. Therefore, it has often been used to measure NLO effects in phthalocyanines and naphthalocyanines.[14,20] Recently, some detailed NLO spectroscopy experiments have been performed that throw additional light on the responsible physical mechanisms. In particular, the effects of metal (Zn, Cu, Pd, Co and Ni) and peripheral substitution on the THG yield of octabutoxy- and octa(decyloxy)-phthalocyanines have been investigated in preliminary experiments at the 1907 nm fundamental wavelength.[100] Similarly, the THG responses for Si, Ge, Sn, Al, Mn and VO naphthalocyanine derivatives have been measured in the spectral range from 1050 to 2100 nm.[101] Clear differences in the values of $\chi^{(3)}$ depending on the central metal have been observed. As for Pcs, the rise in the susceptibility observed at around 1500 nm has been explained in terms of resonance enhancement with a two-photon level below the Q-level transition.

A novel application of spin-coated films is the fabrication of NLO optical waveguides. Recent work on the subject includes picosecond optical bistability in metallophthalocyanine-doped polystyrene waveguides[102] and Z-scan and mode spectroscopy of Pc-doped PMMA waveguides.[103]

Langmuir–Blodgett films. LB films provide unique systems to ascertain the influence of molecular stacking on the third-order NLO response. In pioneering experiments, $\chi^{(3)}$ values of LB films of soluble silicon phthalocyanine were obtained at 602 nm by DFWM.[104] The phase-conjugated signal, which has a resonant character, can be observed even for one-monolayer films. Time-resolved experiments gave information on the dynamics of the DFWM response, which is governed by the presence of bimolecular exciton exciton interactions.

More recently, $\chi^{(3)}$ $(3\omega:\omega, \omega, \omega)$ values have been obtained for LB films of several metallophthalocyanines.[105] Values are not as high as expected from the molecular hyperpolarizabilities,[80,81] possibly due to the particular arrangement of the molecules in the films. It has been shown that the molecules are not lying flat on the substrate, but are tilted and stacked as in a pile of cards, thus reducing the π–π overlapping between adjacent macrocycles. This may account for the reduced susceptibility when the molecules are probed with light propagating perpendicular to the film faces. On the other hand, the data on the effect of metal complexation are very consistent with the discussion presented above on the experiments performed at the molecular level. No significant differences with the central metal are measured at 1064 nm where the resonance at 3ω with the B band is dominant, whereas a large enhancement is found at 1904 nm for the cobalt-containing compound, as for the experiments in solution. In this case the resonance with the d–d two-photon allowed transition at around 1000 nm is causing the enhancement. Therefore, the consistency between the results for solutions and LB films shows that the enhancement in the NLO response is an intrinsic molecular property determined by the molecular energy scheme and not related to the stacking in the films.

THG experiments at 1064 and 1904 nm were performed[106] on LB films of octakis(octylaminocarbonylmethoxy) metallophthalocyanines (related to **11**), which present a high ability to form aggregates by intermolecular hydrogen bonding. Measured $\chi^{(3)}$ values do not show significant differences with respect to the values obtained for compounds **11**, thus pointing out to a small influence of hydrogen bonding on the NLO response.

MBE films. The fabrication of ordered (crystalline) films of Pc is now possible by molecular beam epitaxy (MBE) techniques.[107] This is a very promising route for the preparation of ordered organic structures, not yet sufficiently exploited. An up-to-date review of the state of art of the technique has been recently published.[6] Some of the epitaxial films consist of novel structures that open interesting routes for the preparation of NLO materials. The substrate plays a key role in determining the structure and physical properties of the film. In particular, the effect of the lattice parameter of the substrate on the crystal orientation of vanadyl phthalocyanine (VOPc) films epitaxially grown on KCl–KBr mixed crystals has been clearly assessed.[108] As a consequence, the NLO responses of the films are accordingly modified. One may quote that $\chi^{(3)}$ $(3\omega:\omega, \omega, \omega)$ values of VOPc films epitaxially grown on KBr show almost an order of magnitude enhancement over polycrystalline films deposited on fused silica.[109] Moreover, the epitaxial film presents a clear in-plane anisotropy for the THG yield that is absent in the polycrystalline film.[110] This result highlights the influence of molecular orientation and stacking on third-order NLO behavior.[85] More recently, the THG susceptibilities of both crystalline and amorphous films of VOPc, vanadyl dibenzophthalocyanine (VODBPc) and vanadyl naphthalocyanine (VONc) have been measured.[111] For both types of films, the $\chi^{(3)}$ values were in the order VOPc > VODBPc > VONc.

On the other hand, the potential of multilayers of CuPc and naphthalenetetracarboxylic dianhydride (NTCDA) on KCl for NLO applications has been explored,[112] opening a promising approach for devices having tailored perfomances.

Sol-gel films. Pcs have been incorporated into sol-gel film glasses *via* the sol-gel technique.[113] Because of the relatively low preparation temperature, the method appears quite suitable to host organic molecules in inorganic materials. Few studies of the NLO reponse of these sol-gel systems have so far been performed. The THG susceptibilities of sol-gel hosts containing copper phthalocyanine at molecular concentrations in the range 10^{-4} to 10^{-5} have been measured at 1064 and 1904 nm in as prepared samples as well as after an annealing treatment at 200 °C.[114] On the other hand, the nonlinear self-refraction of gaussian laser beams have been carried out at 532 nm. High values of the third-order susceptibility have been measured.[115]

Nonlinear absorption and refraction: optical limiting behavior

Nonlinear absorption and refraction are closely related NLO effects. In a general case several mechanisms, both parametric and non-parametric, may contribute to these nonlinearities and a reliable assessment of the responsible mechanisms requires experiments involving different pulse lengths. The parametric contributions to the nonlinear response are very small except for very short and intense light pulses and therefore unsuitable for many practical devices. Therefore, the search for nonlinear absorbing materials mostly relies on non-parametric (optical pumping) processes that take advantage of the particular level structure of the system. Due to its practical relevance we will discuss these processes in relation to *optical limiting.*

Optical limiting (OL) is a nonlinear effect consisting of a decrease in the transmittance of a sample under high intensity or fluence illumination. Ideally, the transmitted intensity should remain constant (or even decrease to a small value) above a certain *illumination threshold.* Consequently, the initial constant transmittance should linearly decrease to zero above the threshold. This ideal behavior is illustrated in Fig. 2.

The optical limiting effect finds useful applications for sensor (*e.g.* CCD) protection including the human eye. In a way, optical limiting is the *reverse* of *saturable absorption* (RSA) where an increase in transmittance is observed at high illumination levels. The two nonlinear effects mentioned at the start of the section may contribute to optical limiting, either directly (nonlinear absorption) or through the use of an aperture that

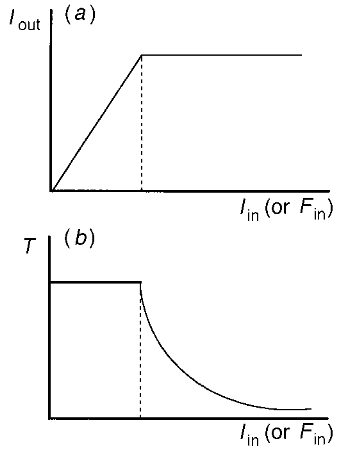


Fig. 2 Ideal behavior of an optical limiter: (*a*) transmitted intensity I_{out} *versus* incident intensity I_{in} (or fluence F_{in}); (*b*) transmittance T *versus* incident intensity (or fluence).

limits the cross-section of the illuminating beam (nonlinear refraction).

Phthalocyanines have been shown to be promising metalloorganic materials for optical limiting in the visible and NIR spectral range, because of their appropriate photophysical properties. Moreover, the spectral bandwidth or window over which the limiter operates can be engineered by altering both the main ring and the peripheral substituents, permiting fine-tuning of the perfomance parameters.

Some useful reviews on the subject, including work on phthalocyanines, have been recently published,[14,20,116–118] so we will focus on the most recent developments.

Dynamics of RSA

Most OL experiments on phthalocyanines and naphthalocyanines are discussed with reference to the five-level scheme shown in Fig. 3. S and T are singlet and triplet states, respectively. Under illumination an initial photon of around 550 nm is absorbed at the ground state level S_0 and takes the molecule to a high vibrational level S_1' of a singlet electronic excited state S_1 (corresponding to the Q band). This state rapidly decays into a lower energy triplet T_1 that may absorb another photon, so that the system is excited to a higher triplet level T_2. Moreover, one-photon transitions from S_1 to a higher lying singlet S_2 are also possible. In accordance with this scheme short-pulse processes are dominated by singlet–singlet absorption before a significant population of the triplet T_1 state has developed. In this case if the cross-section of the S_1–S_2 transition is larger than that for S_0–S_1, *reverse saturation behavior* occurs. Under these conditions the simplest three-level model (S_0, S_1 and S_2) can be used to discuss the results. On the other hand, the processes occurring under long pulse illumination are dominated by triplet–triplet T_1–T_2 transitions. If the corresponding cross-section is larger than that of the S_0–S_1 transition, then *optical limiting* also takes place.

This physical model leads to the following set of rate equations [eqns. (3)–(8)] for the populations of the levels S_0, S_1 and T_1,

$$\mathrm{d}N_0/\mathrm{d}t = -\sigma_0 N_0 I/h\nu + N_1/\tau_1 + N_3/\tau_3 \tag{3}$$

$$\mathrm{d}N_1/\mathrm{d}t = \sigma_0 N_0 I/h\nu - \sigma_1 N_1 I/h\nu + N_2/\tau_2 - N_1/\tau_1 - N_1/\tau_{13} \tag{4}$$

$$\mathrm{d}N_2/\mathrm{d}t = \sigma_1 N_1 I/h\nu - N_2/\tau_2 \tag{5}$$

$$\mathrm{d}N_3/\mathrm{d}t = -\sigma_3 N_3 I/h\nu + N_1/\tau_{13} + N_4/\tau_4 - N_3/\tau_3 \tag{6}$$

$$\mathrm{d}N_4/\mathrm{d}t = \sigma_3 N_3 I/h\nu - N_4/\tau_4 \tag{7}$$

$$N_0 + N_1 + N_2 + N_3 + N_4 = N \tag{8}$$

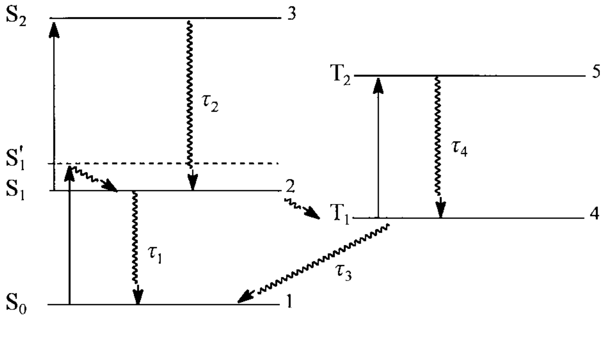


Fig. 3 Schematic diagram showing the levels and relevant transitions for optical limiting action (see text)

where N_i is the population of level i and N the total concentration of molecules, I is the intensity of the light pulse, σ_i the absorption cross-section from level i and τ_i the corresponding lifetimes ($\tau_{13}{}^{-1}$ is the singlet-triplet crossover rate). The optical absorption is given in terms of the populations N_i by eqn. (9).

$$\alpha = \sigma_0 N_0 + \sigma_1 N_1 + \sigma_3 N_3 \tag{9}$$

When $\sigma_3 > \sigma_1 > \sigma_0$ a most favourable situation for optical limiting is obtained. In phthalocyanines and naphthalocyanines, values $\sigma_1/\sigma_0 > 10$ and $\sigma_3/\sigma_0 > 30$ have been achieved.[117] In particular, for pulses shorter than τ_3 but long enough to assure that most molecules are in the strongly absorbing triplet state ($N \cong N_3$) one obtains $\alpha \cong \sigma_3 N I/h\nu$. This absorption is higher than the linear (low fluence) absorption coefficient $\alpha_L = \sigma_0 N I/h\nu$ by the factor $\sigma_3/\sigma_0 \gg 1$.

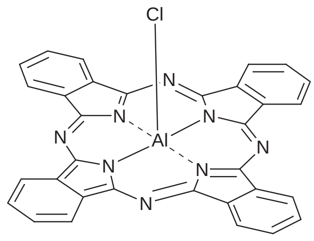
Eqns. (3)–(8) are local in time and space. Therefore, for comparison to experiment they have to be numerically integrated for the duration of the pulse, transversal size of the light beam and sample thickness. The calculations can be made for several wavelengths in order to determine the performance range of the limiter. Recently, powerful beam-propagation methods have been applied to the propagation of light beams in nonlinear absorbing materials.[119]

For enhanced optical limiting performance the photophysical parameters (cross-sections and lifetimes) should be optimized for the particular working conditions of the limiting device.

Relevant experiments

Experiments are usually carried out by focusing a good-quality laser beam onto the liquid or solid sample in order to reach a high intensity. They often use a frequency-doubled Nd:YAG laser at 532 nm, but other wavelengths and a variable wavelength optical parametric oscillator (OPO) have been used to determine the spectral bandwidth.

Molecular level. Phthalocyanine derivatives have received a great deal of attention as reverse saturable absorbers. Optical limiting with phthalocyanines was first reported for chloroaluminium phthalocyanine **15** (CAP).[120]



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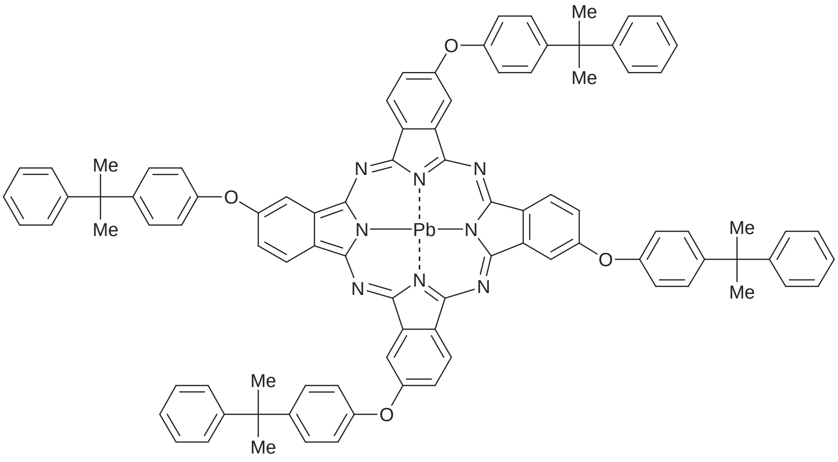
Experiments have been performed on many phthalocyanines in solution, particularly CAP, where much information is available. Much effort is still being devoted to determining the main physical parameters and understanding the relevant mechanisms.[121–123] The role of metal substitution and molecular stacking is being actively investigated,[124] and modified two-dimensional Z-scan methods[125] are being used to improve the experimental information.

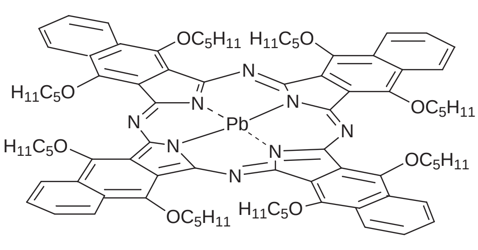
The heavy-atom effect has been exploited to obtain remarkable enhancements in the reverse saturable absorption of phthalocyanines. Several Pc series containing Al, Ga, In and Si, Ge, Sn, Pb as central atoms have been studied.[126] Thus, for example, lead tetrakis(cumylphenoxy)phthalocyanine [PbPc(CP)$_4$] **16** has shown efficient optical limiting performance.[127]



16

The reason for such behavior is that the intercrossing rate from S_1 to T_1 is enhanced for this heavy central metal ion due to the large value of the spin–orbit coupling parameter that couples singlet to triplet states. It has been shown that indium leads to a faster intercrossing rate than lead in spite of its lower atomic number and so improves the limiting threshold.[128] Experiments have also been performed[129] with paramagnetic phthalocyanines such as $VOBu^t_4Pc$ and $Cu(SO_3^-)_4Pc$ sodium salt. It appears that the magnetic moments contribute to the spin–orbit coupling and enhance the intercrossing rate.

A number of naphthalocyanines have been shown to present reverse saturation behavior. Due to the shift of the Q-band to the IR (Fig. 1), the wavelength range is accordingly shifted with regard to that measured for phthalocyanines. For the two kinds of compounds the same general trends with central metal substitution have been observed. In particular, heavy metal ions[130,131] enhance the response due to the higher intercrossing rate. Very promising results have been obtained for lead octa(α-pentoxy)naphthalocyanine **17**.[130] The optical absorption spectrum of a related naphthalocyanine system is shown in Fig. 1, in comparison to that of the related phthalocyanine compounds. Molecular engineering approaches have been used to tune the spectral range of the limiter by donor substitution of naphthalocyanines. It is well-known that the introduction of alkoxy substituents into the α-position of the phthalocyanines and naphthalocyanines drastically shifts the position of the Q-band to higher wavelength.[132–134] Thus, for example, indium and tin octabutoxynaphthalocyanines with red-shifted optical limiting response have been also studied.[135]



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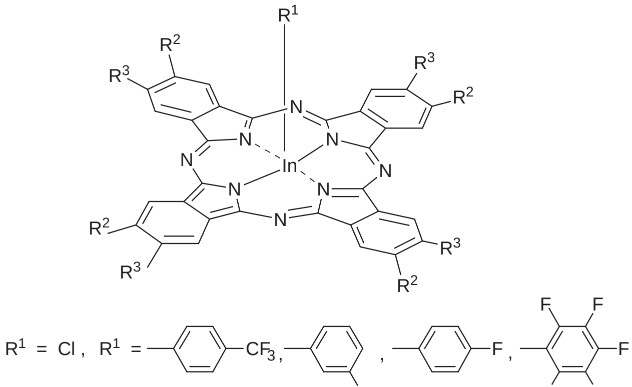
Very recently,[136] Hanack and Heckmann have described the preparation of new highly-soluble axially-substituted indium phthalocyanines **18** especially designed for optical limiting. The optical limiting properties of these compounds are being presently studied.[137]

Materials and devices. Once the most promising molecules for OL behavior have been identified, suitable macroscopic systems should be prepared. Liquids and gels as well as solid host media have been essayed. In principle, liquid solutions[138] present a higher damage threshold due to self-healing, but solid-state materials are more robust and should be preferable for devices. Pc films with a glassy morphology have been obtained by chemically functionalizing the ring periphery *via* amine-epoxy substitution,[139] but the damage threshold is too low. A number of sol-gel host materials containing Pcs have been also investigated.[140–143] Polymer (PMMA), guest–host systems containing either CAP[144] or a silicon phthalocyanine $[PcSi(OC_7H_{15})_2]$ have also been tried.[145] A broadband limiting action has been achieved. One additional advantage of polymer matrixes over liquid hosts is the possibility of achieving a concentration gradient that leads to better overall performances, as mentioned below. A novel approach uses an elastic polymer and viscoelastic gels for guest–host optical limiting matrixes.[146] Additional experiments have shown that an epoxy elastomer has a much higher laser damage threshold than an epoxy glassy thermoset and a PMMA thermoplastic. Silicon naphthalocyanine optical limiting performances have been improved by incorporating the dye into the elastomer host.[147]



R^2 = Bu^t, n-C_5H_{11}

R^3 = H, n-C_5H_{11}

18

From the device point of view, the use of several successive limiters (*tandem* strategy) seems useful to optimize both the overall limiting and damage thresholds in Pcs. Two NcSi solutions have been tested leading to a nonlinear transmission $T_{NL}=0.0017$ and a damage threshold of 8.7 mJ.[148] Signal suppression ratios near 600 have been achieved. Another strategy to optimize the limiter performance makes use of a concentration gradient profile. As an example, it has been shown that a non-homogeneous distribution of indium tetra(*tert*-butyl)phthalocyanine chloride along the beam path enhances the excited-state absorption and leads to an efficient optical limiter.[149] In order to optimize the performance of the limiter different non-homogeneous profiles have been proposed[116] and tested.[150]

Future prospects

Phthalocyanines and related compounds are consolidating their relevant position as optical limiters and third-order NLO materials. Considerable basic photophysical and spectroscopic information has recently been gathered that permits a better understanding of NLO behavior and the role of the central metal ion. Much effort still needs to be devoted to predict the effect of molecular aggregation and supramolecular organization. New materials and strategies to optimize the optical limiting and third-order NLO performance are (and should be) actively pursued. In particular, molecular beam epitaxy, together with the LB technique, should offer enormous perspectives for materials design and fine control of the physical response.

On the other hand, new routes for the synthesis of second-order NLO (*i.e.* non-centrosymmetric) compounds are being implemented. As an example, subphthalocyanines, which are intrinsically unsymmetric compounds, have shown high quadratic hyperpolarizabilities that can be further enhanced by suitable acceptor substitution. This and related approaches could shift the focus of NLO studies from planar (two-dimensional) molecules to more complex three-dimensional systems, where off-diagonal components of the β tensor become very relevant.

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