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Role of Structural Factors in the Nonlinear Optical Properties of Phthalocyanines and Related Compounds

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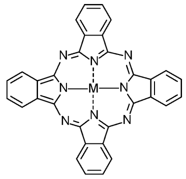
1. Introduction

The field of nonlinear optics (NLO) has been developing for a few decades as a promising field with important applications in the domain of photoelectronics and photonics.[1−3] NLO materials can be used to manipulate optical signals in telecommunication systems and other optical signal processing applications. NLO activity was first found in inorganic crystals,[2,3] such as $LiNbO_3$, but the choice of these materials is rather limited. Also, most of them have either low NLO responses (e.g. semiconductors) or important drawbacks for processing into thin films and being incorporated into micro-optoelectronic devices (e.g. ferroelectric crystals). By the mid-1980s, organic materials emerged as important targets of choice for nonlinear optical applications[4−11] because they exhibit large and fast nonlinearities and are, in general, easy to process and integrate into optical devices. Moreover, organic compounds offer the advantage of tailorability: a fine-tuning of the NLO properties can be achieved by rational modification of the chemical structure. Finally, they are ideal to achieve the ultimate goal of device miniaturization by going into the molecular level.

Strong nonlinearities in organic molecules usually arise from highly delocalized π-electron systems. Phthalocyanines[12−16] (Pcs) **1**, with their extensive two-dimensional 18 π-electron system, fulfill this requirement and have been, indeed, intensively investigated as NLO materials.[6,17−20] They exhibit other additional advantages, namely, exceptional stability, versatility, and processability features. The architectural flexibility of phthalocyanines is well exemplified by the large number of metallic complexes described in the literature, as well as by the huge variety of substituents that can be attached to the phthalocyanine core. Furthermore, some of the four isoindole units can be formally replaced by other heterocyclic moieties, giving rise to different phthalocyanine analogues.[15] All these chemical variations can alter the electronic structure of the macrocyclic core, and therefore, they allow the fine-tuning of the nonlinear response.



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Aside from their practical interest, Pc-related molecules present very attractive features for fundamental NLO studies. Since the unsubstituted and many substituted compounds are planar (2D, two-dimensional), they offer the possibility of investigating the role of dimensionality on the NLO response. In fact, 2D molecules represent the next step in complexity when their perfomance is compared to that of the mostly investigated linear (1D, one-dimensional) compounds. Whereas these molecules are characterized by a single component β_{zzz} of the hyperpolarizability tensor, 2D molecules present, under Kleinman symmetry, two diagonal, β_{zzz} and β_{xxx}, and two off-diagonal, β_{zxx} and β_{zzx}, components of the $\boldsymbol{\beta}$ tensor. Very large ratios β_{zxx}/β_{zzz} have been calculated for a number of two-dimensional sytems.[21] Also, comparable values of β_{zxx} and β_{zzz} have been found for octupolar molecules such as crystal violet and several ruthenium complexes.[22,23] Consequently, the correlation between structure and NLO response is much richer for 2D than for 1D molecules and offers more variables for optimization. Moreover, the additional degrees of freedom associated with 2D

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Purificación Vázquez, born in 1951, studied chemistry at the Autonoma University of Madrid (UAM) and received a doctorate in 1981, working in Natural Products Chemistry within the group of Prof. J. Borges. After a postdoctoral stay with Prof. D. Arigoni (ETH, Zürich), she joined in 1983 the Autonoma University of Madrid as Assistant Professor, starting work in Supramolecular Chemistry with Prof. J. de Mendoza. In 1985 she was promoted to her current position of Associate Professor in Organic Chemistry. Since November 1991 she has been in the group of Prof. T. Torres. Her present research interest is focused on the synthesis of Molecular Materials Based on Phthalocyanines and Related Compounds and the study of their properties, such as nonlinear optical, photophysical, and electrical properties, and applications, as well as on the study of structure–property relationships.

structures may allow a finer tuning of the NLO response.

By introducing peripheral substituents or by core modification, one can alter the point-group symmetry and the ratio between off-diagonal and diagonal tensor components. In fact, for 2D molecules one can go from purely dipolar to purely octupolar behavior and so examine the role of multipolarity on the response. Moreover, by adding axial substituents, one may obtain three-dimensional (3D) structures with pyramidal shape and examine the effect of a third dimension on the NLO response. In any case, NLO measurements provide sensitive and meaningful tests to evaluate theoretical models of the geometrical and electronic structure.

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Born in 1951 in Madrid, Tomás Torres is currently Full Professor and Director of the Department of Organic Chemistry at the Autonoma University of Madrid (UAM). He received his Ph.D. (1978) at the same University, working at the Spanish National Research Council (CSIC) in Madrid (Prof. Fariña). After two years (1978–80) at the Department of Organic Chemistry and Spectroscopy of the Max-Planck-Institute for Biochemistry, in Martinsried near Munich (Germany, Prof. Dr. W. Schaefer), as a Max-Planck Society postdoctoral fellow, he joined (1981–85) a private company, Abello S. A.–Merck, Sharp and Dohme, as Senior Researcher, in Madrid. In 1985 he was appointed to the staff of the Autónoma University of Madrid. In addition to various aspects of synthetic, heterocyclic, and supramolecular chemistry, his current research interests include the synthesis of low-symmetry phthalocyanines and the preparation and study of the photophysical and nonlinear optical properties of molecular materials based on phthalocyanines and related compounds. He is now responsible for a research group of three permanent researchers and about 12 graduate students and postdoctoral fellows. He is the author or coauthor of over 200 research papers and patents.

Regarding the processability for yielding useful macroscopic structures, it is possible to build up thin films of many Pcs and porphyrins by several techniques (spin coating,[24] molecular beam epitaxy,[25] Langmuir–Blodgett (LB) technology[24]). In a number of cases, useful low-loss optical waveguides have been produced, allowing the fabrication of competitive nonlinear integrated optics devices.[26] In fact, many Pc-related compounds present an optical transmission window in the blue-green region of the spectrum. Therefore, ordered films might be used to generate this short wavelength visible light by frequency doubling near-infrared (IR) radiation. Third-order processes, such as third-harmonic generation (THG) and, particularly, degenerate four-wave mixing (DFWM), are also possible and can be applied to a variety of devices for communications and computing such as frequency converters, optical switches, phase-conjugated mirrors, logical gates, and so forth. The advantage with regard to second-order processes is that they do not require any molecular ordering and can even be applied to centrosymmetric compounds. This avoids device degradation associated with orientational relaxation of the poled films. Finally, the electronic structure of Pcs and porphyrins appears adequate for optical limiting applications, and interesting perspectives are already opened.

This review arises from the need to compile the important advances obtained in the field of the NLO properties of phthalocyanines and analogues. Far from giving an exhaustive description of all the work that has been done in this area,[17] we will focus on the main new trends. Whereas for 1D systems such as polyenes the correlation between structure and NLO response is relatively well developed, much progress is recently being achieved for 2D systems such as Pcs and porphyrins. Such questions as the role of molecular symmetry and multipolar character, metal complexation, peripheral and axial substitution, and core modification are addressed.

2. Brief Survey of Nonlinear Optics

The effect of a light wave on a material is usually described through the induced electrical polarization **P**. At low irradiation intensities, this polarization is a linear function of the wave field **E**,

$$\mathbf{P} = \chi^{(1)}\cdot\mathbf{E} \qquad (1)$$

where $\boldsymbol{\chi}^{(1)}$ is the linear susceptibility.

However, when the material is subjected to an intense light field (i.e. a laser light), the polarization is no longer a linear function of the applied field. Then, the nonlinear polarization can be expressed by

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

where $\boldsymbol{\chi}^{(2)}$ and $\boldsymbol{\chi}^{(3)}$ are, respectively, the quadratic (first-order) and cubic (second-order) susceptibilities, parameters that determine the magnitude of the second- and third-order nonlinear optical responses. At the molecular level, a similar equation can be written for the light-induced molecular dipole moment,

$$\mathbf{p} = \alpha\cdot\mathbf{E} + \beta\cdot\mathbf{EE} + \gamma\cdot\mathbf{EEE} + ... \qquad (3)$$

with the coefficients $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and $\boldsymbol{\gamma}$ being the linear polarizability, the first (quadratic) hyperpolarizability, and the second (cubic) hyperpolarizability, respectively. The susceptibilities and polarizabilities (hyperpolarizabilities) are second-rank ($\boldsymbol{\chi}_{ij}{}^{(1)}$ or $\boldsymbol{\alpha}_{ij}$), third-rank ($\boldsymbol{\chi}_{ijk}{}^{(2)}$ or $\boldsymbol{\beta}_{ijk}$), and fourth-rank ($\boldsymbol{\chi}_{ijkl}{}^{(3)}$ or $\boldsymbol{\gamma}_{ijkl}$) tensors. In the most general case, they have, respectively, 9, 27, and 71 components. However, under off-resonant conditions, Kleinmann symmetry is obeyed and the tensors are invariant versus any permutation of subindices. Moreover, geometrical symmetries may further reduce the number of independent nonzero components. In particular, odd-rank tensors, such as β, are identically zero for centrosymmetric systems, that is, having inversion symmetry. On the other hand, the components of all those tensors are functions of the frequencies of all wave fields mixed by the nonlinear process. The frequency dependence is considered through the usual notation $\boldsymbol{\alpha}(\omega;\omega)$, $\boldsymbol{\beta}(\omega;\omega_1,\omega_2)$, $\boldsymbol{\gamma}(\omega;\omega_1,\omega_2,\omega_3)$, where ω is the output frequency and ω_i are the input ones. A similar nomenclature applies to the susceptibilities. As an example, for second-harmonic generation (SHG) the responsible hyperpolarizability writes $\boldsymbol{\beta}(2\omega;\omega,\omega)$, and for third-harmonic generation (THG) the corresponding hyperpolarizability is $\boldsymbol{\gamma}(3\omega;\omega,\omega,\omega)$. When one of those frequencies or a combination of them coincides with one of the *eigenfrequencies* of the medium, the corresponding nonlinearity undergoes a strong enhancement (*resonance*). For SHG, resonances appear at ω and 2ω, whereas, for THG, they take place at ω, 2ω, and 3ω.

The above class of electronic nonlinearities, often called *parametric*, is extremely fast, on the subpicosecond regime, since the response time is that required for the electrons to redistribute under the influence of the applied field. They correspond to *virtual* optical transitions and obey strict *phase-matching* rules. Second- (SHG) and third-harmonic generation (THG) belong to this type of nonlinearities and are used to generate coherent radiation in the transparent range of the nonlinear medium. The macroscopic susceptibilities $\boldsymbol{\chi}^{(n)}$ can be derived from the microscopic hyperpolarizabilities by a suitable average over all the possible molecular orientations in the system (see refs 4 and 5).

A main aim of the molecular NLO field is to predict the values of $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ for a given chemical structure. This prediction constitutes the basis for the optimization of the microscopic NLO perfomance. The most widely used model to discuss the NLO perfomance of organic molecules is based on a perturbation expansion of the Stark energy under an applied field. The expansion consists of a summation over the electronic states of the system (SOS: sum over states). One of the main advantages of the method stems from the fact that in many cases only a few electronic levels contribute significantly to the NLO response. Then, the frequency dispersion response is clearly apparent. Moreover, the parameters appearing in the expansion are directly linked to the electronic structure through the energy of the eigenstates and the transition matrixes among them. The general SOS expressions for the components of the

$\boldsymbol{\beta}$ and γ tensors are well-known.[27] One should be aware that for centrosymmetric molecules not only one-photon (parity-allowed) transitions contribute to the sum but also parity-forbidden (two-photon) transitions that do not appear in the optical (linear) absorption spectra.

Regarding $\boldsymbol{\beta}$, the general expressions simplify for the particular relevant cases where the contribution of a few levels is dominant. For 1D charge-transfer molecules (such as *p*-nitroaniline) a two-level model has yielded satisfactory results for the quadratic hyperpolarizability. For planar (2D) systems, such as most Pcs and analogous compounds, three levels (or even more) are generally required to account for $\boldsymbol{\beta}$. However, for strongly push−pull molecules with a dominant optical absorption (Q) band, a two-level model may still be a reasonable approximation. As a relevant case for this review, we will consider the second-order response in a three-level model (the ground 0 and the excited 1 and 2 levels, responsible for the Q band). For some unsymmetrically substituted push−pull compounds, one may assume C_{2v} symmetry due to the presence of the charge-transfer axis z and write for the nonzero quadratic hyperpolarizability components

$$\beta_{zzz} = \beta_{33} = \frac{(\mu_{01}^{z})^2 \Delta\mu_{01}^{z}}{\hbar^2} d_{33}$$

$$\beta_{zxx} = \beta_{31} = \frac{(\mu_{02}^{x})^2 \Delta\mu_{02}^{z}}{\hbar^2} d_{31} + \frac{2\mu_{01}^{z}\mu_{02}^{x}\mu_{12}^{x}}{\hbar^2} d_{31} \tag{4}$$

$$\beta_{xxz} = \beta_{15} = \frac{(\mu_{02}^{x})^2 \Delta\mu_{02}^{z}}{\hbar^2} d_{15} + \frac{\mu_{02}^{x}\mu_{12}^{x}\mu_{01}^{z}}{\hbar^2} d_{15}$$

where the dispersion factors are

$$d_{33} = \frac{3\omega_{01}^2}{2(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)}, \quad d_{31} = \frac{1}{2(\omega_{02}{}^2 - \omega^2)},$$

$$d'_{31} = \frac{\omega_{01}\omega_{02} + 2\omega^2}{2(\omega_{01}^2 - 4\omega^2)(\omega_{02}^2 - \omega^2)},$$

$$d_{15} = \frac{\omega_{02}^2 + 2\omega^2}{2(\omega_{02}^2 - 4\omega^2)(\omega_{02}^2 - \omega^2)},$$

$$d'_{15} = \frac{1}{2(\omega_{01}^2 - \omega^2)} \left\{ \frac{\omega_{01}\omega_{02} + 2\omega^2}{(\omega_{02}^2 - 4\omega^2)} + \frac{\omega_{01}\omega_{02} - \omega^2}{(\omega_{02}^2 - \omega^2)} \right\} \tag{5}$$

In these expressions ω_{01} and ω_{02} stand for the peak frequencies of the two relevant optical transitions, μ_{01}, μ_{02}, and μ_{12} refer to the optical transition moments, and $\Delta\mu_{01}$ and $\Delta\mu_{02}$ refer to the change in electrical dipole moment when the molecule is excited from the ground state to the 1 or 2 excited states, respectively. Damping factors have been neglected. When states 1 and 2 coincide, one goes from the three- to the two-level model and the corresponding expressions are

$$\beta_{zzz} = \beta_{33} = \frac{(\mu_{01}^{z})^2 \Delta\mu_{01}^{z}}{\hbar^2} d_{33}$$

$$\beta_{zxx} = \beta_{31} = \frac{(\mu_{01}^{x})^2 \Delta\mu_{01}^{z}}{\hbar^2} d_{31} \tag{6}$$

$$\beta_{xxz} = \beta_{15} = \frac{(\mu_{01}^{z})^2 \Delta\mu_{01}^{z}}{\hbar^2} d_{15}$$

For a linear (1D) molecule, $\mu_{01}^{x} = 0$ and the only nonzero component of the $\boldsymbol{\beta}$ tensor is

$$\beta_{zzz} = \beta_{33} = \frac{\mu_{01}^{2} \Delta\mu_{01}}{\hbar^2} d_{33} \tag{7}$$

which for $\omega = 0$ reduces to the well-known expression

$$\beta_{zzz}^{(0)} = \frac{3\mu_{01}^{2} \Delta\mu_{01}}{2\omega_{01}^{2}\hbar^2} \tag{8}$$

so that

$$\beta_{zzz}(2\omega;\omega,\omega) = \beta_{zzz}^{(0)} d_{33} \tag{9}$$

Concerning the cubic hyperpolarizability, the corresponding SOS expressions for γ_{ijkl} are much more complicated than those for $\boldsymbol{\beta}$. The simplest two-level model expression for the average $\langle\gamma(3\omega;\omega,\omega,\omega)\rangle$ responsible for THG in an isotropic molecular assembly is

$$\langle\gamma(3\omega;\omega,\omega,\omega)\rangle = \mu_{01}^{2}\Delta\mu_{01}^{2} d_{11} - \mu_{01}^{4} d'_{11} \tag{10}$$

where d_{11} and d'_{11} are dispersion factors.[28] Although such an expression is too simple to account for THG behavior in Pcs and Pc-related compounds, it exhibits some clues of this third-order response. It consists of an asymmetric polar term (positive at low frequencies) and a centrosymmetric term (negative at low frequencies). The competition between these two contributions determines the sign of the off-resonant (low-frequency) cubic hyperpolarizability. At variance with $\boldsymbol{\beta}$, several levels generally contribute to this nonlinearity because of the effect of the resonances at ω, 2ω, and 3ω.

It is sometimes convenient to decompose the $\boldsymbol{\beta}$ and γ tensors into irreducible spherical multipolar components.[29,30] The decomposition is particularly useful for the second-order nonlinearity. When Kleinman symmetry applies, that is, under off-resonant conditions, the decomposition for $\boldsymbol{\beta}$ is as follows

$$\boldsymbol{\beta} = \boldsymbol{\beta}_{J=1} \oplus \boldsymbol{\beta}_{J=3} \tag{11}$$

where $\boldsymbol{\beta}_{J=1}(\beta_{1,-1},\beta_{1,0},\beta_{1,1})$ and $\boldsymbol{\beta}_{J=3}(\beta_{3,-2},\beta_{3,-1},\beta_{3,0},\beta_{3,1},\beta_{3,2})$ stand for the *vector* (*dipolar*) and *octupolar* components of the $\boldsymbol{\beta}$ tensor.

For the simplest case of 1D molecules along the z axis, they reduce to

$$\beta_{1,0} = [2/(15)^{1/2}]\beta_{zzz}, \quad \beta_{1,\pm 1} = 0$$

$$\beta_{3,0} = [2/(10)^{1/2}]\beta_{zzz}, \quad \beta_{3,\pm 3} = \beta_{3,\pm 2} = \beta_{3,\pm 1} = 0 \quad (12)$$

and for 2D molecules in the ZX plane

$$\begin{aligned} \beta_{1,0} &= [2/(15)^{1/2}](\beta_{zzz} + \beta_{zxx}), \\ \beta_{1,1} &= -\beta_{1,-1} = -[3/(30)^{1/2}](\beta_{xxx} + \beta_{xzz}) \\ \beta_{3,\pm 3} &= [\pm 1/2(2)^{1/2}](-\beta_{xxx}) \\ \beta_{3,\pm 2} &= [2/(3)^{1/2}]\beta_{zxx} \qquad (13) \\ \beta_{3,\pm 1} &= [\pm 3/2(30)^{1/2}](\beta_{xxx} - 4\beta_{xzz}) \\ \beta_{3,0} &= [1/(10)^{1/2}](2\beta_{zzz} - 3\beta_{zxx}) \end{aligned}$$

One should note that if $\beta_{J=1} = 0$ (octupolar symmetry) the molecule does not possess any permanent dipole moment even if it still presents second-order activity associated with $\beta_{J=3}$. In comparison to dipolar systems, octupolar molecules may present an improved nonlinearity−transparency tradeoff. However, since they present multidirectional charge transfer, the simple two-level model is clearly not valid.[31] Octupolar symmetries are D_{3h}, T_d, and 222.

The multipolar formalism reveals an interesting differential feature between 1D and 2D molecules. For linear molecules the ratio between the norms of the dipolar and octupolar terms (*anisotropy ratio*) is fixed at $^1/_3$. On the other hand, for 2D molecules one can go from purely dipolar ($\beta_{J=3} = 0$) to purely octupolar ($\beta_{J=1} = 0$) systems, providing a way to study the role of multipolarity on the quadratic NLO response.

The next step after an efficient NLO molecule has been synthesized is to produce a suitable macroscopic arrangement that ensures a large macroscopic response. In the case of the second-order response, one needs a non-centrosymmetric molecular assembly. This is usually achieved by poling a molecular solution or a spin-coated film to induce a preferential alignment, but also through crystal growth, LB deposition, and molecular beam epitaxy. For the third-order response, the correlation between structure and response is less clear, and there is still much work to do.

Finally, there are *nonparametric or incoherent* NLO processes relying on light-induced changes in the population of the energy levels of the molecules (*optical pumping*) which result in changes of the optical properties of the medium. They cannot be adequately described by optical susceptibilities and may give rise to large NLO responses. Phase-matching restrictions do not apply. The response times are generally much larger than those for the parametric processes and depend on the lifetimes of the involved transitions. An illustrative example of such nonlinearities is provided by the so-called *saturable absorption*; that is, the absorption coefficient becomes saturated at high light intensities. This behavior occurs whenever a light beam interacts with a two-level system. Efficient optical limiting phenomena, to be described in section V, also rely mostly on these types of processes. Here, three or more levels could participate in the process.

3. Second-Order NLO Processes

Recent years have witnessed a growing interest in the search for materials with large macroscopic second-order nonlinearities[23,32,33] because they are of great practical utility as frequency doublers, frequency conversors, and electro-optic modulators[34] by means of second-harmonic generation, parametric frequency conversion (or mixing), and the electro-optic effect. They are respectively described by $\chi^{(2)}(2\omega;\omega,\omega)$, $\chi^{(2)}(\omega;\omega_1 \pm \omega_2)$, and $\chi^{(2)}(\omega;0,\omega)$. The search for these materials requires, in a first step, the optimization of the microscopic parameter β by using non-centrosymmetric charge-transfer molecules. In many organic compounds the second-order optical nonlinearity arises from a highly polarizable π-conjugated system capped with groups of different electron affinities. Such dipolar polarizable molecules exhibit one dominant hyperpolarizability component lying in the direction of the charge-transfer axis. Representative examples of these dipolar one-dimensional molecules are the donor−acceptor (push−pull) disubstituted polyenes.[35] For 2D and 3D compounds, the available data are more scarce and the rationale for the measured NLO behavior is still in a very preliminary stage. Although high values have been determined or calculated for β, in only a few cases they approach the best 1D values.

The most widely used experimental technique for the determination of the hyperpolarizability in organic molecules is electric-field-induced second-harmonic generation (EFISH)[36−39] in solution. Since SHG cannot occur in an isotropic solution, poling with a strong external electric field is used to create a partially non-centrosymmetric macroscopic structure. EFISH measures the third-order $\chi^{(3)}(2\omega;0,\omega,\omega)$ susceptibility through the Maker fringes obtained in a liquid cell with thick windows in the wedge configuration. This susceptibility includes both an electronic (generally neglected) γ_e and an orientational γ_o contribution. The later one, associated with the preferential orientation of the molecules by the field, is given by

$$\gamma_o = \frac{\mu\beta_v}{5kT} \qquad (14)$$

where $\beta_v = \beta_1$ is the vector (dipolar) component of the tensor. Assuming that the electronic term is negligible, one immediately determines the projection of this vector on the dipole moment if its magnitude is known. It should be noted that the neglect of the electronic contribution is not always justified for highly polarizable compounds and should be checked for each particular case.[40]

Since 1980 a new technique based on hyper-Rayleigh light scattering (HRS)[41−44] has been available. In this experiment, the incoherently scattered

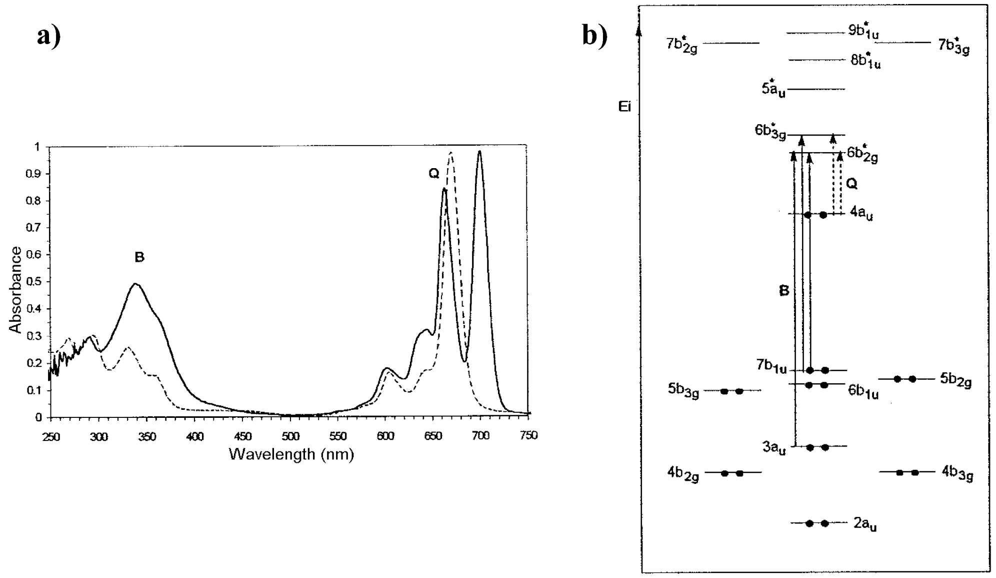


Figure 1. (a) Typical UV−vis spectra of metallophthalocyanines (dotted line) and metal-free phthalocyanines (continuous line). (b) Electronic transitions accounting for B and Q bands of phthalocyanines.

frequency-doubled light arising from the SHG active molecules is detected. Although the material may be macroscopically isotropic, the correlation between local fluctuations induces a detectable second-harmonic light. Then, the intensity of the second-harmonic scattered light is proportional to the orientational average $\langle \beta_{ijk}\beta_{lmn}\rangle$, and one writes

$$I_{2\omega} = GN \sum_{ijklmn} \langle \beta_{ijk}(2\omega;\omega,\omega)\beta_{lmn}(2\omega;\omega,\omega)\rangle (I_{\omega})^2 = GN\langle \beta^2_{\mathrm{HRS}}\rangle (I_{\omega})^2 \quad (15)$$

This expression provides the definition for β_{HRS}. It depends on the polarization of the fundamental and harmonic beams, providing a means to determine different components of the $\boldsymbol{\beta}$ tensor. As compared to EFISH, the advantage of this technique is that it can be applied to ionic and nonpolar molecules. In particular, this technique has enabled experimental determination of the hyperpolarizability of octupolar molecules,[29,30,45,46] that can exhibit nonzero $\boldsymbol{\beta}$. However, one should be aware that, to obtain meaningful data, careful experiments should be performed that avoid the spurious contribution of multiphoton excited luminescence. Several techniques have been developed to achieve this objective.[47,48]

From the technological side, the goal is to produce suitable macroscopic molecular structures that yield high values of the quadratic susceptibility. In the ideal limit of complete molecular orientation (and ignoring local field effects), $\boldsymbol{\chi}^{(2)} = N\boldsymbol{\beta}$, with N being the molecular concentration. Macroscopic $\boldsymbol{\chi}^{(2)}$ susceptibilities have been measured in oriented (e.g. spin-coated) films, single crystals, and epitaxial films. Measurements are based on the method of the Maker fringes as for EFISH in solution. The film sample is rotated around an axis perpendicular to the incidence plane of the fundamental beam. The SHG intensity is determined[49] as a function of the rotation angle θ.

It should be noted that for a meaningful comparison of (either $\boldsymbol{\beta}$ or $\boldsymbol{\chi}^{(2)}$) data by different authors the values should be extrapolated to $\omega = 0$ (*off-resonant values*) in order to correct for the dispersion factors. This is not often easy, since it requires a theoretical model that provides a definite functional expression for the wavelength dispersion factors.

3.1. Second-Order NLO Activity in Phthalocyanines

The main ingredient to account for the NLO response of a molecule is its scheme of electronic energy levels. In accordance with their electronic structure, Pcs present intense $\pi-\pi$ bands in the visible (Q band) and UV (B or Soret band) spectral regions that mostly determine the NLO response (Figure 1a). The electronic level structure of Pcs has been investigated by several authors. Figure 1b illustrates the results of VCH calculations[50] for unsubstituted Pcs. Q and B bands correspond to transitions to the lowest excited-state orbitals (e_g) from the highest occupied orbital a_u (for the Q band) and from the low occupied b_{1u} and a_u orbitals (for the B band). For metal-free phthalocyanines, the Q band is split into two main components while metal-containing phthalocyanines with D_{4h} symmetry exhibit only a single Q band in their visible spectra (Figure 1a). The exact position of these bands depends on the particular structure, metal complexation, and peripheral substituents.[12,16] Metal incorporation induces a decrease in the extinction coefficient for the Q (and B) band. For peripherally substituted metallic Pcs (e.g. push−pull compounds), the degenerate Q bands show some splitting due to the reduction in symmetry. The broad absorption valley between the B and Q bands could be used for frequency doubling into the green spectral region.

For porphyrins, the absorption spectra show also B (centered at around 400 nm) and Q (between 480 and 700 nm) bands, but they present some relevant differential features (Figure 2a). In particular, the Q bands show much smaller oscillator strength than the B band. It is commonly accepted that those bands

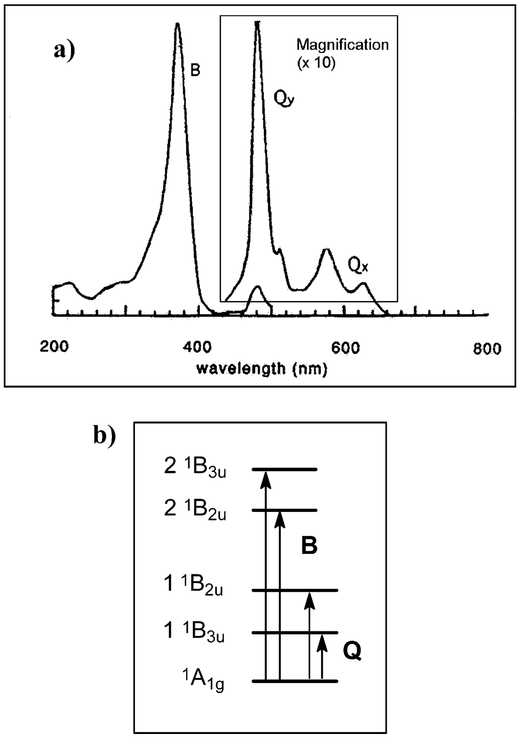


Figure 2. (a) Typical UV–vis spectrum of metal-free porphyrins. (b) Electronic transitions accounting for B and Q bands of porphyrins.

primarily derive from transitions between the highest occupied molecular orbitals, HOMO and HOMO-1, and the two lowest unoccupied molecular orbitals, LUMO and LUMO+1 (four-orbitals model). For the free-base porphyrins, these orbitals are a_{1u}, b_{1u}, b_{2g}, and b_{3g}, respectively. The low-energy excited states (1^1B_{2u}, 1^1B_{3u}, 2^1B_{2u}, and 2^1B_{3u}) are mostly made up of one-electron transitions involving those orbitals. It has been proposed that the Q band is associated with ^1A_g (ground state) $\rightarrow$ 1^1B_{3u}, 1^1B_{2u} transitions with a low oscillator strength and that the B band is associated with $^1A_g \rightarrow 2^1B_{3u}$, 2^1B_{2u} transitions, as schematically illustrated in Figure 2b. In metalloporphyrins, the excited states become degenerated into 1^1E_{1u} and 2^1E_{1u}.

It is valuable to comment here on the UV–vis spectra of other related Pc analogues, such as naphthalocyanines, higher homologues of phthalocyanines with extended π-conjugation, and subphthalocyanines, lower analogues formed by three isoindole units around a central boron atom. Naphthalocyanines show a marked shift of the bands toward longer wavelengths with regard to phthalocyanines, whereas subphthalocyanines exhibit a Q band centered at around 600 nm.

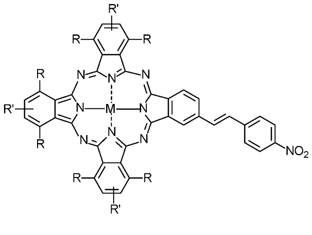
Two- and three-level models have been mostly used to account for the second-order NLO behavior of phthalocyanines. They include either the doubly degenerate or split excited levels responsible for the sharp Q band.

As mentioned above, only non-centrosymmetric molecules are able to yield second-harmonic generation, so that in principle, the intrinsically centrosymmetric phthalocyanines do not fulfill the main requirement for second-order chromophores. However, phthalocyanines bearing suitable donor and acceptor substituents in the same molecule were proposed more than a decade ago as promising candidates for second-order nonlinear optics.[51] From then on, some reports on NLO experiments over push–pull phthalocyanines have been published. This approach is quite attractive, since it permits us to modulate the NLO response as a function of the peripheral substitution. Considering the enormous variety of substituents that can be attached to the periphery of the macrocyclic core, exhaustive studies can be carried out, by varying the donor–acceptor substitution pattern, the electron-donor or -acceptor strength of the substituents, or even the central metal while keeping the peripheral groups. In fact, it has been recently discussed how the metallic atom can alter the electronic structure of the molecule and tune the NLO response.[52] Also, theoretical calculations[53] on the electronic structure and second-order nonlinear optical properties of differently substituted phthalocyanines can provide useful information for the design of efficient chromophores.

However, the synthesis of unsymmetrically substituted phthalocyanines is an arduous task.[54,55] Different methods have been described for the preparation of this type of derivatives, but the most usual one is the statistical condensation of two differently substituted precursors (A and B), namely, phthalonitriles or 1,3-diiminoisoindolines. This approach affords a statistical mixture of six phthalocyanines, from which only the AAAB, BBBA, and AABB derivatives are capable of behaving as second-order materials. Commonly, the precursors are mixed up in a 3:1 (A/B) ratio, to favor the formation of the unsymmetrical derivative bearing three identical and one different isoindole subunits (AAAB derivatives), that can be isolated from the mixture by chromatographic techniques. However, AABB type derivatives are not readily obtained using this method, since it is usually difficult to separate them from their structural isomers: the centrosymmetric ABAB macrocycles. Some selective approaches lead to these AABB derivatives,[56−58] but their applicability is limited to only a few peripheral substituents. For this reason, phthalocyanines comprising three electron-donor and one electron-withdrawing groups or *vice versa* have been the preferred targets to study the second-order nonlinear behavior,[17,18] even though AABB derivatives were initially predicted as high-performance second-harmonic generators.

The first studies on the microscopic nonlinear responses of unsymmetrically substituted phthalocyanines were reported in 1996.[59] The experiments were accomplished by the EFISHG technique,[59,69] but no evidence of relevant β was found. In these reports, both the donor and acceptor functional groups were directly attached to the Pc core. The approach followed by some authors in order to enhance the quadratic hyperpolarizabilities is the extension of the conjugation pathway. It is well-known that an increase in the number of double or triple bonds between the donor and acceptor groups in linear systems (up to a certain saturation limit) results in an enhancement of the second-order NLO response.[61]

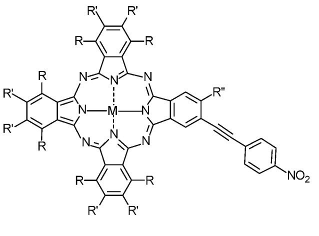
Considering this fact, some authors decided to prepare phthalocyanines bearing π-delocalized electron-acceptor substituents,[62,63] which induce an extended π-conjugation length. Thus, a set of phthalocyanines **2** were prepared for studying the influence of the position and electronic character of the substituents, as well as the role of the central metal atom, on the second-order NLO properties of phthalocyanines with extended conjugation.



2a R = H, R' = $C(CH_3)_3$, M = 2H
b R = H, R' = $C(CH_3)_3$, M = Cu
c R = H, R' = $C(CH_3)_3$, M = Co
d R = H, R' = $C(CH_3)_3$, M = Ni
e R = C_8H_{17}, R' = H, M = Ni
f R = OC_8H_{17}, R' = H, M = Ni

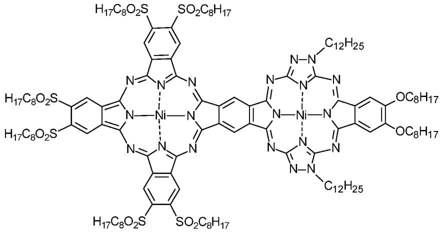
EFISH experiments were performed to obtain the off-resonant dipolar $\beta_v(0)$ component of the $\boldsymbol{\beta}$ tensor.[40] First of all, it is worth mentioning that all the values are quite significant, the larger one being a $\beta_v(0)$ value of $\sim 50 \times 10^{-30}$ esu. Additionally, some interesting structure−activity relationships were inferred from the experimental results. The extension of the conjugation path to the acceptor NO_2 group definitely enhances the second-order NLO response. Moreover, an increase in the hyperpolarizability is observed on increasing the metallic ion polarizability.

The efficacy of the π-electronic extension approach is confirmed by the work developed by Wada, Sasabe, and co-workers, who prepared push−pull phthalocyanines bearing exocyclic conjugated nitro groups, such as **3a**.[64−66] The authors reported that films of these derivatives show larger SH signals than those composed of phthalocyanines in which the nitro group is directly attached to the phthalocyanine core.[64,65] Moreover, EFISH and HRS experiments have been performed on solutions of phthalocyanines **3b** and **3c**, bearing one and two 4-nitrophenylethynyl moieties as the acceptor component of the push−pull system.[67] The β_{HRS} and β_{EFISH} values obtained from the experiments are exceptionally high, particularly for the zinc derivative of **3c**, whose β_{HRS} value can be estimated to be $\sim 550 \times 10^{-30}$ esu. These values are the largest found for push−pull phthalocyanines and offer a route of optimization of the SHG response.



3a R = R' = OCH_2CF_3; R'' = H
b R = H; R' = OBu; R'' = H
c R = H; R' = OBu; R'' = $-C\equiv C-C_6H_4-NO_2$

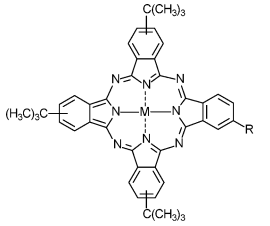
Although the introduction of linear π-conjugated substituents seems to positively affect the second-harmonic generation capability of phthalocyanines, the extension of the conjugation by means of fusing another macrocyclic unit to the Pc core does not render an increase in the second-order response. This is the conclusion of the experiments carried out on phthalocyanine−triazolehemiporphyrazine dimers **4**.[68] The presence of the triazolehemiporphyrazine core seems to interrupt the effective charge transfer between the electron-donor and electron-withdrawing components.



4

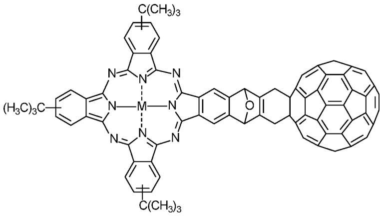
A number of studies have also been performed on macroscopic Pc systems. As a first remark, one should mention that Hoshi and co-workers found fairly strong SHG from thin films[69−72] and discotic phases[73] of metal-free phthalocyanine and some centrosymmetric metallic complexes despite their centrosymmetry. After the analysis of different possible mechanisms, the authors considered that an electrical quadrupole transition can rationalize the observed phenomenon. Another interesting observation was the SHG response from the symmetrically substituted tetrakis(cumylphenoxy)phthalocyanine,[74] with the random disposition of the voluminous peripheral groups being responsible, in this case, for the second-order effect. Some efforts have also been directed to the study of vanadyl phthalocyanine (VOPc).[75] The V═O bond in this molecule is perpendicular to the molecular plane, so this derivative is non-centrosymmetric and polar. Very recently, several titanium(IV),[76] gallium(III),[76] and indium(III) phthalocyanines[77] axially substituted by different ligands have been measured by EFISH and HRS. The axial group induces asymmetry and provides the molecule with an axial dipole moment. The three components of the susceptibility tensor have also been obtained from spin-coated films.[77]

Liu, Wada, and Sasabe were the pioneers in measuring SHG on thin films of AAAB unsymmetrically substituted phthalocyanines.[78,79] They prepared non-centrosymmetric Z-type and alternated LB films of nitro-tri-*tert*-butylphthalocyanine. It is remarkable that a very high value of the second-order susceptibility was found for the copper derivative **5a** ($\chi^{(2)} = 2 \times 10^{-5}$ esu). More recently, the same authors have reported the characterization and SHG of Z-type LB films of 1,8-naphthalimide-tri-*tert*-butylphthalocyanine **5b**.[80] However, the susceptibility value obtained from the three-layer film is not so high as that previously found for the nitro-substituted counterpart **5a** ($\chi^{(2)} = 8.3 \times 10^{-9}$ esu). This result is reasonable, since the charge-transfer process should be more effective in the former derivative.



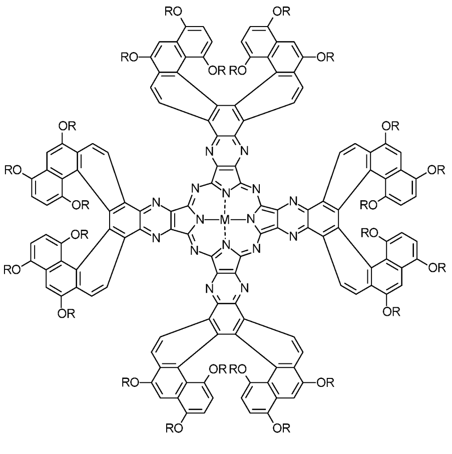
5a R = NO_2
b R = naphthalimide

Second-order response has also been tested in LB films of a phthalocyanine−fullerene dyad **6**.[81] C_{60} is a fascinating molecule with excellent electron-accepting properties. Considering the electronic characteristics of the phthalocyanine core, phthalocyanine−C_{60} dyads[82−85] are excellent candidates for studying the second-harmonic generation. Preliminary studies show an increase of the SH signal with the number of layers on the LB film, a fact that proves the existence of an intrinsic second-order nonlinear optical property of the material. Further interpretation of the experimental results has to be done.



6

Another interesting result at the macroscopic level is that obtained with LB films of molecules in which the cores of metal octaazaphthalocyanines are fused to four nonracemic helicenes **7**.[86] These compounds stack in solution and in the solid state, giving rise to chiral superstructures. Langmuir and Langmuir−Blodgett films of these helical derivatives also show stacks of molecules, with the stacking axes parallel to the surface. Although the molecules are symmetrically substituted, the LB films show a second-order nonlinear optical response. For molecules with this D_4 symmetry, the only nonzero components of the quadratic hyperpolarizability tensor and, therefore, of the first-order susceptibility are those associated with chirality. However, the experimental susceptibility values are notably larger than expected, considering the contribution of only one of the components of the $\boldsymbol{\chi}$ tensor (χ_{xyz}). This result is in agreement with the previously reported enhancement of the second-order nonlinear optical response in supramolecular arrays of chiral molecules with regard to the monomeric species.[87]



7a R = $C_{12}H_{25}$; M = Cu
b R = $C_{12}H_{25}$; M = Ni

Experimental data for $\boldsymbol{\beta}$ and $\boldsymbol{\chi}^{(2)}$ are summarized in Table 1. Values as high as 530 × 10^{-30} esu (at λ = 1.064 μm) have been measured for the quadratic hyperpolarizability of some unsymmetrically substituted compounds (**3c**). On the other hand, the largest $\boldsymbol{\chi}^{(2)}$ (30 × 10^{-9} esu at λ = 1.064 μm) has been measured on LB monolayers, highlighting the potential of this technique to achieve a high degree of molecular ordering. Only in a few cases, EFISH and HRS data have been reported for the same compound (**3b** and **3c**) and at the same wavelength. Moreover, very few data points have been obtained at more than one wavelength in order to have a good assessment of the dispersion factors.

3.2. Second-Order NLO Activity in Phthalocyanine Analogues

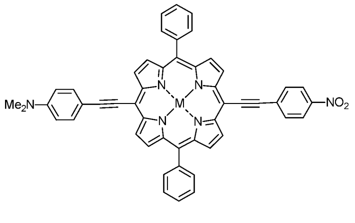
Porphyrins present similar electronic characteristics to those of Pcs as NLO materials. Earlier studies on this type of macrocycles were carried out by Suslick and co-workers at the beginning of the 90s.[88] They examined the NLO properties of a set of *meso*-substituted porphyrins with both 4′-(dimethylamino)-phenyl and 4′′-nitrophenyl moieties. These push−pull porphyrins were measured by the EFISH technique and showed β values of 10−30 × 10^{-30} esu. These and other related metalloporphyrins[89−91] specifically tailored for quadratic NLO responses exhibit moderate molecular hyperpolarizabilities due to the dihedral twist of the *meso*-phenyl rings with respect to the porphyrin core,[90] which limits to some extent the efficient coupling between donor and acceptor moieties. It has been theoretically predicted by Marks et al.[92] that the insertion of π-electron spacer groups, such as alkenyl or alkynyl moieties, between the phenyl groups and the porphyrin skeleton may enlarge the NLO response. These computational results are in agreement with the experiments[93] and calculations[94] performed by Therien and co-workers on structures such as **8**, in which the electron donor, acceptor, and linker are essentially coplanar, enabling effective electronic interactions within the molecule. Particularly, the copper derivative possesses exceptionally high resonance-enhanced β values, near 5000 × 10^{-30} esu, obtained by the HRS technique. This hyperpolarizability value is the largest yet measured for an organic chromophore, but one has to note that it is 10-fold larger than the theoretically predicted value using INDO/SCI calculations.[94]

With the aim of understanding the structure−property relationship of this class of chromophores, new materials based on the 5,15-diphenylporphyrin core have been prepared and their second-order NLO properties tested.[95] For example compound **9**, bearing the strong donor dimethylaminophenylethynyl and

Table 1. Second-Order Nonlinear Parameters for Selected Phthalocyanines

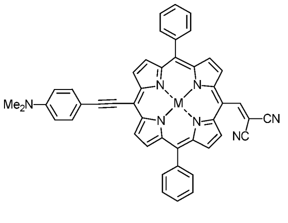
compd	$\chi^{(2)}$ ($\times 10^{-9}$ esu)	β ($\times 10^{-30}$ esu)	$\beta(0)$ ($\times 10^{-30}$ esu)	λ (μm)	technique	condensed phase/ solution	ref
2a			40.9	1.907	EFISH	$CHCl_3$ solution	40
2b			28.1	1.907	EFISH	$CHCl_3$ solution	40
2c			40.2	1.907	EFISH	$CHCl_3$ solution	40
2d			44.0	1.907	EFISH	$CHCl_3$ solution	40
2e			39.7	1.907	EFISH	$CHCl_3$ solution	40
2f			13.6	1.907	EFISH	$CHCl_3$ solution	40
3b		220		1.064	HRS	$CHCl_3$ solution	67
		−162		1.064	EFISH	$CHCl_3$ solution	
		41.1		1.907	EFISH	$CHCl_3$ solution	
3c		530		1.064	HRS	$CHCl_3$ solution	67
		−384		1.064	EFISH	$CHCl_3$ solution	
		522		1.907	EFISH	$CHCl_3$ solution	
4		2.82		1.907	EFISH	$CHCl_3$ solution	68
$(^t\mathrm{Bu})_3(\mathrm{NO}_2)\mathrm{PcH}_2$	30	3		1.064	SHG	LB monolayer	77
$(^t\mathrm{Bu})_3(\mathrm{NH}_2)\mathrm{PcH}_2$	33	5.90		1.064	SHG	LB monolayer	79
5b	8.32	5.97		1.064	SHG	three-layer LB film	80
PcZn	5.9			1.122	SHG	vacuum-deposited film	72
PcVO	5.0			1.186	SHG	vacuum-deposited film	72
PcTiO	4.8			1.198	SHG	vacuum-deposited film	72
PcPb	1.4			1.210	SHG	vacuum-deposited film	72
PcSn	1.4			1.306	SHG	vacuum-deposited film	72
$(\mathrm{C}_5\mathrm{H}_{12})\mathrm{PcIn{-}Cl}$		−35.5	25.0	1.064	EFISH	$CHCl_3$ solution	76
	0.19[a]			1.064	SHG		
	0.20[b]						
	0.50[c]						
$(\mathrm{C}_5\mathrm{H}_{12})\mathrm{PcIn{-}Ph}$		−56.5	27.0	1.064	EFISH	$CHCl_3$ solution	76
	0.23[a]			1.064	SHG	poled PMMA[h] film	
	0.28[b]						
	1.00[c]						
$(\mathrm{C}_5\mathrm{H}_{12})\mathrm{PcIn{-}}p\mathrm{CF}_3\mathrm{C}_6\mathrm{H}_4$		−53.7	35.5	1.064	EFISH	$CHCl_3$ solution	76
	0.33[a]			1.064	SHG	poled PMMA film	
	0.39[b]						
	13.0[c]						
7a	24[d]			1.064	SHG	five-layer LB film	86
	3[e]						
	4[f]						
	6[g]						
7b	19[d]			1.064	SHG	five-layer LB film	86
	4[e]						
	3[f]						
	15[g]						

[a] $\chi^{(2)}_{15}$. [b] $\chi^{(2)}_{31}$. [c] $\chi^{(2)}_{33}$. [d] χ_{xyz}. [e] χ_{xxz}. [f] χ_{zxx}. [g] χ_{zzz}. [h] PMMA, poly(methyl methacrylate).



8a M = Cu
b M = Zn

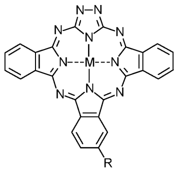
the well-known acceptor dicyanoethenyl moiety, and other related counterparts have been measured by means of the HRS technique, following the previous studies on porphyrins **8**. The authors found two-photon fluorescence, so they employed the alternative EFISH method to evaluate the dipolar β value, that turned out to be quite high, ~125 × 10^{-30}. In light of these and other findings, previous reported results should be revised for excluding the multiphoton excited luminescence contribution to the β values. A recent work on other unsymmetrically functionalized porphyrins bearing nitro and alkoxy groups, measured by EFISH and THG, does not address any estimation of β values, since the authors consider that the high magnitude of γ_{THG} does not allow us to ignore the contribution of the cubic electronic term to γ_{EFISH}. However, the authors have observed that the coordination to metal ions does not disturb much the γ_{EFISH} response.[96]



9

Another type of structures based on the porphyrin core has been recently tested, namely, a porphyrinato−porphyrazinato zirconium sandwich complex,[97] but its off-resonance hyperpolarizability related to second-harmonic generation is very small. Regarding symmetrically substituted compounds, cationic porphyrins adsorbed at a water/1,2-dichloroethane interface have been studied by the SHG technique.[98] At variance with expectations, these species generate intense SH signals, suggesting that the electronic structure of the molecules at the interface is modified with regard to that in the bulk state.

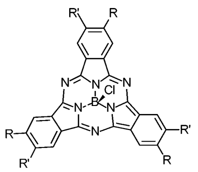
Triazolephthalocyanines[99] **10** are macrocycles isoelectronic to phthalocyanines that arise from the formal substitution of one of the isoindole units comprising the Pc core by a 1,2,4-triazole one. One of the advantages of these derivatives from the second-order NLO activity point of view is that they are intrinsically unsymmetrical derivatives and possess a permanent dipolar moment along the plane of the molecule. Moreover, they can be synthesized by a stepwise approach,[100] that allows the ready introduction of both electron donor and acceptor groups in the same molecule, which can enhance the charge-transfer processes and, therefore, improve the nonlinear optical response.



10a R = $C(CH_3)_3$
b R = OC_8H_{17}

Thus, the intrinsic dipolar moment of the molecule is increased by the introduction of donor groups in the isoindole moiety opposite to the triazole one. Compounds **10a** and **10b** have $\mu = 6.5$ and 13 D, respectively. HRS and EFISH experiments have been performed on solutions of these derivatives.[101] β_{HRS} values are significantly high, 110 and 80×10^{-30} esu, respectively, thus evidencing the strong potential of this type of materials for second-order NLO. When comparing the β_{HRS} and β_{EFISH} values, one may note that there is an increase in the ratio $\beta_{EFISH/HRS}$ upon moving from compound **10b** to **10a**. This increase was associated with a change in the direction of the transition dipole moment, from almost perpendicular to parallel with regard to the molecular axis. From this observation, it was concluded that the relative importance of the off-diagonal and diagonal components of β and of the dipolar and octupolar contributions can be controlled through chemical manipulation of the triazolephthalocyanine core, as a function of the electronegativity and geometrical arrangement of the substituents. Interesting calculations showing this kind of effect on the hyperpolarizability components of porphyrins were also reported.[94] Owing to the above-mentioned feature, the significant SHG response, and the fact that these macrocycles can be organized in non-centrosymmetric condensed phases,[102] triazolephthalocyanines may be considered as attractive building blocks for NLO applications.

Another type of high-performance second-order molecules is the intrinsically unsymmetrical Pc analogues called subphthalocyanines (**11**).[103] Subphthalocyanines are cone-shaped 14-π-electron aromatic macrocycles, which consist of three isoindole units containing a boron atom with an axial halogen ligand in the macrocyclic cavity. Preparation of subphthalocyanines is carried out by condensation reaction of the appropriate phthalonitriles in the presence of BCl_3 or BBr_3.



11 a R = H; R' = NO_2
b R = H; R' = I
c R = H; R' = SO_2-alkyl
d R = H; R' = S-alkyl
e R = R' = SO_2-alkyl
f R = R' = S-alkyl

Pioneer NLO experiments with subphthalocyanines by the groups of Zyss, Agulló-López, and Torres pointed out the possibility that these compounds may predominantly behave as octupolar molecules. The high β_{HRS} values first reported[104] were revised and compared with the hyperpolarizability values obtained by HRS on molecules **11a**−**11f**.[105] The best performance corresponded to compound **11e**, which exhibits a $\beta_{HRS} = 260 \times 10^{-30}$ esu. This value is higher than that calculated for the octupolar TATB molecule[46] and also than those measured for the Ru chiral compounds,[106,107] tris(2,2′-bipyridil)ruthenium^{II} bromide hexahydrate (RuTB) and tris(1,10-phenanthroline)ruthenium^{II} chloride hexahydrate (RuTP), although it is smaller than those of some optimized trisubstituted Ru complexes.[22] However, the EFISH yield from the investigated SubPc molecules was found to be very low, thus evidencing that the measured β should be mostly associated with the octupolar component, in accordance with the expected behavior. This result is also reasonable, since theoretical calculations indicate that the apical halogen does not significantly contribute to the low-energy optical transitions (Q and B bands) mostly responsible for the NLO response. Then, the second-order response is determined by light-induced charge transfer inside the basal macrocycle presenting D_{3h} octupolar symmetry. In other words, one can ignore the halogen atom on the top of the macrocycle and deal with a planar molecule.

Persoons et al. have more recently tackled the HRS measurements in solution of hexasubstituted subphthalocyanines **11f**.[108−110] They have measured a series of thioalkylsubphthalocyanines differing in the alkyl chain length. All of them show average fluorescence-free β values of $\sim 190 \times 10^{-30}$ esu, similar to those previously reported.[105]

On the other hand, the second-harmonic generation response of unsubstituted subnaphthalocyanines (SubNcs) was measured for the first time by EFISH and HRS experiments.[111] The quadratic hyperpolarizability derived from the experiments is similar ($\boldsymbol{\beta}$HRS(0) = 34.7 × 10−30 esu) to that also measured under the same conditions for the related unsubstituted subphthalocyanine.

A challenging target for all the researchers working in this area is to establish the relationship between the microscopic and the macroscopic second-order behavior. One of the advantages of these nearly octupolar molecules is the existence of a dipole moment along the B−Cl axis, which allows the preparation of non-centrosymmetrical spin-coated films via corona poling. SHG experiments have been

Table 2. Second-Order Nonlinear Parameters for Selected Phthalocyanine Analogues

compd[a]	$\chi^{(2)}$ ($\times 10^{-9}$ esu)	β ($\times 10^{-30}$ esu)	$\beta(0)$ ($\times 10^{-30}$ esu)	λ (μm)	technique	condensed phase/ solution	ref
(dmap)(np)$_3$PorH$_2$[b]		10		1.064	EFISH	CHCl$_3$ solution	88
(dmap)$_2$(np)$_2$PorH$_2$[b]		30		1.064	EFISH	CHCl$_3$ solution	88
(dmap)$_3$(np)PorH$_2$[b]		20		1.064	EFISH	CHCl$_3$ solution	88
(p-NMe$_2$C$_6$F$_4$)(p-NO$_2$C$_6$F$_4$)PorH$_2$		54		1.064	HRS	C$_2$H$_4$Cl$_2$ solution	90
(p-NMe$_2$C$_6$F$_4$)(p-NO$_2$C$_6$F$_4$)PorZn		92		1.064	HRS	C$_2$H$_4$Cl$_2$ solution	90
(p-NMe$_2$C$_6$F$_4$)(p-NO$_2$C$_6$F$_4$)PorCu		118		1.064	HRS	C$_2$H$_4$Cl$_2$ solution	90
8a[c]		4374		0.83	HRS	CHCl$_3$ solution	93
		1501		1.064			
8b[c]		5142		0.83	HRS	CHCl$_3$ solution	93
		4933		1.064			
9		124		1.907	EFISH	CHCl$_3$ solution	95
(Por)Zr(Porz)[d]		0.45		1.907	EFISH	CH$_2$Cl$_2$ solution	97
10a		−103		1.907	EFISH	CHCl$_3$ solution	101
		110		1.34	HRS		
10b		−24		1.907	EFISH	CHCl$_3$ solution	101
		80		1.34	HRS		
11a		144.3		1.46	HRS	CHCl$_3$ solution	105
11b		164.5		1.46	HRS	CHCl$_3$ solution	105
11c		168.5		1.46	HRS	CHCl$_3$ solution	105
11d		76.5		1.46	HRS	CHCl$_3$ solution	105
11e		260		1.46	HRS	CHCl$_3$ solution	105
11f		40		1.46	HRS	CHCl$_3$ solution	105
11f		190	21	1.30	HRS	CHCl$_3$ solution	109, 110
11a	−0.20[e]	−4[h]		1.064	SHG	poled PMMA film	112
	0.43[f]	9[i]					
	0.03[g]	0.4[j]					
11b	−0.26[e]	−2[h]		1.064	SHG	poled PMMA film	112
	0.57[f]	5[i]					
	0.03[g]	−0.3[j]					
11c	−0.31[e]	−9[h]		1.064	SHG	poled PMMA film	112
	0.77[f]	29[i]					
	0.11[g]	0[j]					
SubNc			34.7	1.064	HRS	CHCl$_3$ solution	111

[a] Por, porphyrin ring. [b] dmap, p-(dimethylamino)phenyl; np, p-nitrophenyl. [c] Probably, these values are enhanced by two-photon fluorescence phenomena. [d] Porz, porphyrazine ring. [e] $\chi^{(2)}_{15}$. [f] $\chi^{(2)}_{31}$. [g] $\chi^{(2)}_{33}$. [h] $\beta^{(2)}_{15}$. [i] $\beta^{(2)}_{31}$. [j] $\beta^{(2)}_{33}$.

performed on spin-coated films of **11a**, **11b**, and **11c**.[49,112] These experiments have allowed a determination of the three nonzero elements of the $\boldsymbol{\chi}^{(2)}{}_{ij}$ tensor. The $\chi^{(2)}{}_{31}$ component is the highest, opposite to the case of linear molecules, which show a dominant $\chi^{(2)}{}_{33}$ value. From the susceptibilities, an evaluation of the components of the $\boldsymbol{\beta}$ tensor was carried out through the statistical connection between the microscopic and macroscopic responses. The analysis led to a value of the axial component β_{33} very close to zero, which is in agreement with the results found at the microscopic level.

Following the studies on the macroscopic response of condensed phases, authors have also reported the organization of appropriately functionalized subphthalocyanines in Langmuir−Blodgett films, as well as preliminary studies on their second-order NLO behavior.[113] SHG experiments have been carried out on Y-type LB films of subphthalocyanine **11c** and alternated films using compound **11c** and behenic acid. The former yields small but appreciable SHG when the observation and illumination angles are ~50° with regard to the normal to the film, but no SHG signal could be detected for a p-polarized beam, thus indicating a non-centrosymmetric ordering restricted to the first transferred layers. However, a larger SHG was measured for the alternated LB films, which is consistent with a non-centrosymmetric molecular ordering through the whole film.

The measured $\boldsymbol{\beta}$ and $\boldsymbol{\chi}^{(2)}$ values for Pc-related compounds are summarized in Table 2. Much higher values of β than those of Pcs have been measured for compounds **8a** and **8b** by HRS. Also EFISH values for several molecules (**9** and **10a**) are quite remarkable. For the other compounds, values are moderate and similar to those of Pcs. On the other hand, the $\boldsymbol{\chi}^{(2)}$ values measured in poled spin-coated films are rather low.

4. Third-Order NLO Processes

As mentioned in section II, there is a larger variety of third-order processes and susceptibilities[114] in comparison with second-order ones. Parametric processes include third-harmonic generation, $\boldsymbol{\chi}^{(3)}(3\omega;\omega,\omega,\omega)$, four-wave mixing, $\boldsymbol{\chi}^{(3)}(\omega;\omega_1,\omega_2,\omega_3)$, intensity-dependent refractive index (nonlinear refraction), $\boldsymbol{\chi}^{(3)}(\omega;\omega,-\omega,\omega)$, and Kerr electrooptic effects, $\boldsymbol{\chi}^{(3)}(\omega;0,0,\omega)$. There are also nonparametric processes such as thermal, photochromic, and photorefractive effects and a variety of optical-pumping effects. Each process can be associated with one or various mechanisms whose relative importance depends on experimental conditions (wavelength, pulse length). The main techniques[44] that have been used for Pcs and related compounds are third-harmonic generation (THG),[115] degenerate four wave mixing (DFWM),[116] and Z-scan.[117] The EFISH method can be also utilized to ascertain the cubic molecular hyperpolarizabilities. THG measures $\chi^{(3)}(3\omega:\omega,\omega,\omega)$ and exclusively involves electronic mechanisms. This technique, like EFISH, uses a liquid cell with thick windows in the wedge configuration. The intensity of the THG signal is measured as a function of cell translation (Maker fringes). Moreover, by measuring the concentration dependence of the harmonic light as a function of the molecular concentration, both the real (γ') and imaginary (γ'') components of the complex hyperpolarizability ($\gamma = \gamma' + i\gamma''$) can be determined.[118]

Degenerate four-wave mixing (DFWM) involves the nonlinear mixing of three waves of frequency ω to generate a fourth wave of the same frequency. The intensity of this signal wave is measured as a function of the input intensities in order to obtain the responsible third-order susceptibility, $\chi^{(3)}(\omega;\omega,\omega,-\omega)$, which accounts for several relevant processes. One of them is *two-photon absorption* (TPA), corresponding to simultaneous absorption of two photons and described by the imaginary part of that susceptibility at the resonant frequency 2ω. In this case, the optical transition connects states of the same parity with energy separation $2\hbar\omega$. Consequently, the absorption coefficient $\alpha = \alpha_1 + \beta I$ is made up of the linear term α_1 (due to one-photon transitions) and of a nonlinear (intensity-dependent) term $\alpha_2\beta$, associated with the two-photon absorption. [Note that the nolinear absorption coefficient and the quadratic hyperpolarizability are represented by the same symbol (β).] On the other hand, the real part is responsible for a nonlinear contribution to the refractive index (n_2I) that adds to the linear value n_1. This nonlinear term, known as the *optical Kerr effect*, accounts for several interesting processes such as wave self-focusing and self-phase modulation. In esu, the relation between n_2 and $\chi^{(3)}(\omega;\omega,-\omega,\omega)$ is

$$n_2 = \frac{16\chi^{(3)}}{c\pi^2\epsilon} \tag{16}$$

One particularly interesting geometry uses two counterpropagating (pump) waves and a probe wave that generates its phase-conjugated (time-reversed) wave. Phase conjugation has a number of peculiar features that find interesting applications in adaptative optics, image processing, and laser technologies.

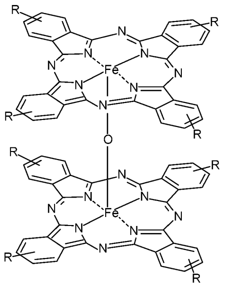
Z-scan experiments measure the nonlinear refractive index (NLR) by focusing a Gaussian beam onto a cell containing the solution of chromophores. The optical transmittance through the cell is measured as a function of sample position with regard to the focal point. Similar scans using an open aperture yield the nonlinear absorption (NLA). From the NLR and NLA one can determine the sign and the magnitude of both the real and imaginary parts of $\chi^{(3)}(-\omega:\omega,\omega,-\omega)$. This technique is mainly employed to study the optical limiting behavior of phthalocyanines, as we will discuss below. At variance with THG, DFWM and Z-scan are sensitive to nonelectronic mechanisms (thermal, ...). Therefore, for third-order effects, one must be especially careful when comparing data obtained by different techniques. Also, even using the same technique, differences in the wavelength and pulse length of the fundamental beam may give rise to different results due to the different dispersion laws and time scales (dynamics) associated with each particular mechanism.

4.1. Third-Order NLO Activity in Phthalocyanines

Phthalocyanines have been extensively studied for their third-order NLO properties both in solution and as thin films. The theoretical analysis of the experimental data is more complicated than that for second-order processes and generally demands models involving four electronic levels due to the role of the 2ω and 3ω resonances at the Q and B bands, respectively. The model involving the ground 0 state and the 1 (Q band) and 2 (B band) excited states and a two-photon state 3 (one-photon transitions are parity-forbidden) has been found satisfactory to account for the response of centrosymmetric Pcs. Detailed calculations of the third-order hyperpolarizabilities have been recently reported.[119,120]

The role of the central metal atom has been investigated in some experiments.[121−125] Incorporation of transition metals seems to strongly enhance the off-resonant $\chi^{(3)}$. Particularly, a clear enhancement of the cubic hyperpolarizability has been observed for phthalocyanines containing cobalt,[121,124] and the result has been justified on the basis of its uncompleted d-shell character. This result appears to be in accordance with the model developed by di Bella[52] predicting that open-shell complexes should show larger hyperpolarizabilities than closed-shell metal compounds. However, to reach a sound conclusion, more systematic data on the spectral dependence of the nonlinear response are needed in order to properly take into account the effect of frequency dispersion factors. THG experiments of spin-coated thin films of octaalkoxyphthalocyanines[126] and naphthalocyanines[127] also throw some light on the effects of metal substitution. In most cases, the one-, two-, or three-photon resonance contribution accounts for the large third-order optical nonlinearities.

The effect of transition and rare-earth metals (M = Sc, Lu, Yb, Y, Gd, Eu, Nd) on γ was investigated some years ago in sandwich-type bis(phthalocyanines) by means of DFWM.[128] The γ values were 1 order of magnitude larger than those of the typical metallophthalocyanines, as expected for such highly delocalized systems. The differences found in this series of compounds clearly point to resonance effects. Other sandwich-type phthalocyanines, such as Sm(Pc)$_2$ and Eu(Nc)$_2$ (Nc = naphthalocyanine) have also shown higher γ values than mononuclear derivatives in DFWM experiments,[129,130] the Nc derivative being the one with the larger hyperpolarizability value. This fact supports the theory of the larger electron delocalization to explain the increased nonlinear coefficients in sandwhich-type phthalocyanines. Titanium bisphthalocyanine solutions have also been studied using the Z-scan technique, but the results did not supply additional information on this kind of systems.[131] More recently, DFWM measurements over solutions of μ-oxo dimeric iron(III) phthalocyanines **12** have been reported.[132] The figure of merit values $\chi^{(3)}/\alpha$ are among the best reported so far in phthalocyanine systems, and the second hyperpolarizabilities are similar to those obtained for sandwich complexes.

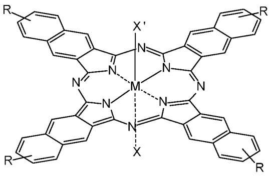


12 a R = H
b R = OC_6H_{13}
c R = $C(CH_3)_3$

Considering the larger γ values obtained from experiments with μ-oxo dimers or sandwich complexes, it is reasonable to believe that molecular stacking can lead to enhancements of the third-order response. In fact, theoretical analyses have found two possible mechanisms that are responsible for the increase in the γ values on going from the monomers to dimers or trimers.[133] This analysis is in agreement with DFWM experiments, which showed a strong enhancement of γ for PcSiO oligomers as a function of the number of macrocycles.[134] However, the experiments performed on spin cast films of ruthenium(III) phthalocyanine-based oligomers, which possess diisocyanobenzene ligands as bridges between the Pc units, revealed that the NLO response was mainly determined by the individual cores.[135] In this case, there is no interaction between the macrocycles, owing to the presence of this large type of bridging ligands. The comparison of the two experiments mentioned above brings out that $\pi-\pi$ overlapping between the macrocycles may be the origin of the enhancement, with the intermolecular electronic interaction giving rise to a supramolecular NLO response. Likewise, the aggregation effect also enhances the macroscopic third-order nonlinearity of phthalocyanines, as shown recently by Sasabe et al. with experiments performed on hexadecakis-substituted phthalocyanines.[136]

It is also well-known that the introduction of peripheral substituents can tune the third-order NLO response, since they alter in some stage the electronic structure of the macrocycle. In this regard, a set of molecules peripherally functionalized with donor and acceptor groups has been studied by means of THG and EFISH experiments.[60] A clear correlation of the hyperpolarizability with the Hammet parameter was obtained, revealing that γ becomes maximal for molecules that have either strong donor or acceptor groups. Z-scan experiments over a family of μ-oxo-titanium phthalocyanines also show that the peripheral substitution with electron-rich moieties leads to an enhancement of the calculated γ values when working with on-resonance conditions.[137]

On the other hand, the effect of the extension of the π-conjugation on the third-order NLO response has been evaluated by Nalwa.[138,139] THG experiments over thin films of phthalocyanine[138] and naphthalocyanine[139] (**13**) derivatives clearly demonstrated that third-order optical nonlinearity increases with the enlargement of the π-electron conjugation. Additionally, THG susceptibilities of MBE films of vanadyl phthalocyanine (VOPc), vanadyl dibenzophthalocyanine (VODBPc), and vanadyl naphthalocyanine (VONc) have been measured and the values found were in the order VOPc > VODBPc > VONc.[140] In this case, the observed trend could be explained by the quality of the prepared films rather than by electronic effects on the particular molecules.



13

A recent and effective approach that leads to enlarged third-order optical nonlinearities is the formation of charge-transfer complexes. The $C_{60}-Pc$ adduct **6** combines the unique acceptor characteristics of fullerene with the donor features of the phthalocyanine. Time-resolved optical Kerr gate experiments show that the second-order hyperpolarizability of the CuPc-C_{60} adduct[141] is 5.4×10^{-31} esu, larger than the values previously reported for most monomeric phthalocyanines, thus evidencing the efficacy of this route. Following the same approach, Langmuir−Blodgett films of a donor−acceptor heterocomplex based on Zn(II) porphyrinate and metal-free phthalocyanine have been prepared and their nonlinear optical properties evaluated.[142] Moreover, a supramolecule based on a phthalocyanine and an anthraquinone unit exhibits an enhancement of the molecular hyperpolarizability as a consequence of the charge transfer between the two chromophores after optical excitation.[143]

Experiments have also been performed on thin films. In most cases, the measured behavior is consistent with that found at the molecular level. Experiments have been carried out on sublimated,[144,145] spin-coated,[126,127,146,147] Langmuir−Blodgett,[142,148,149] and molecular beam epitaxy (MBE)[140,150−155] films as well as on composites.[156] For example, the same enhancement of cobalt-containing phthalocyanines found for experiments in solution[121] takes place in the LB film.[148] However, the average values measured for this series of metallophthalocyanines in the films[148] are not as high as expected from the molecular hyperpolarizabilities, probably due to the particular arrangement of the molecules that reduces the $\pi-\pi$ overlapping between macrocycles. This fact points out the influence of the molecular ordering on the NLO response of phthalocyanine assemblies. An interesting feature of ref 144 is that it reports a detailed study of the dispersion behavior of THG from 950 to 2000 nm. The wavelength dependence of both the modulus and phase of $\chi^{(3)}$ was determined. The data for the unsubstituted Pcs were satisfactorily explained by a four-level model including an even parity state (responsible for

Table 3. Third-Order Nonlinear Parameters for Selected Phthalocyanines

compd	$\chi^{(3)}$ ($\times 10^{-12}$ esu)	$\chi^{(3)}/\alpha$ ($\times 10^{-15}$ esu·cm)	γ ($\times 10^{-32}$ esu)	λ (mm)	technique	condensed phase/ solution	ref
$(cumph)_4PcH_2$[a]	4			1.064	DFWM	$CHCl_3$ solution	122
$(cumph)_4PcPb$[a]	20			1.064	DFWM	$CHCl_3$ solution	122
$(cumph)_4PcPt$[a]	200			1.064	DFWM	$CHCl_3$ solution	122
$(C_8H_{17})_2NCOCH_2OPcH_2$			4.57	1.34	THG	$CHCl_3$ solution	121
			0.92	1.064	EFISH	$CHCl_3$ solution	121
	0.62			1.064	THG	LB film	148
$(C_8H_{17})_2NCOCH_2OPcCu$			2.45	1.34	THG	$CHCl_3$ solution	121
			3.94	1.064	EFISH	$CHCl_3$ solution	121
	0.34			1.064	THG	LB film	148
$(C_8H_{17})_2NCOCH_2OPcNi$			3.18	1.34	THG	$CHCl_3$ solution	121
			2.47	1.064	EFISH	$CHCl_3$ solution	121
	0.42			1.064	THG	LB film	148
$(C_8H_{17})_2NCOCH_2OPcCo$			4.48	1.34	THG	$CHCl_3$ solution	121
			4.39	1.064	EFISH	$CHCl_3$ solution	121
	0.57			1.064	THG	LB film	148
$(t\text{-}Bu)_4NcVO$[b]	3.41	3.30		1.50	THG	spin-coated film	127
$(t\text{-}Bu)_4NcAlClOH$[b]	1.41	1.36		1.50	THG	spin-coated film	127
$(t\text{-}Bu)_4NcMn(COCH_3)_2$[b]	3.32	0.47		1.50	THG	spin-coated film	127
$(OC_4H_9)_4NcSn[OSi(C_2H_5)_3]_2$[b]	2.07	2.40		1.50	THG	spin-coated film	127
$(SC_{10}H_{21})_4NcSi[OSi(C_2H_5)_3]_2$[b]	56.0	1.60		1.50	THG	spin-coated film	127
$(CO_2C_5H_{11})_4NcGe[OSi(C_4H_9)_3]_2$[b]	18.6	14.91		1.50	THG	spin-coated film	127
$(t\text{-}Bu)_4PcGe(OH)_2$	10.5			1.50	THG	spin-coated film	138
Pc_2Sc		60	48	1.064	DFWM	$CHCl_3$ solution	128
Pc_2Lu		100	34	1.064	DFWM	$CHCl_3$ solution	128
Pc_2Yb		100	41	1.064	DFWM	$CHCl_3$ solution	128
Pc_2Y		200	26	1.064	DFWM	$CHCl_3$ solution	128
Pc_2Gd		200	22	1.064	DFWM	$CHCl_3$ solution	128
Pc_2Eu		200	22	1.064	DFWM	$CHCl_3$ solution	128
Pc_2Nd		100	15	1.064	DFWM	$CHCl_3$ solution	128
Pc_2Sm	0.18	375	43.6	0.532	DFWM	DMF solution	130
Nc_2Eu[b]	0.16	290	55	0.532	DFWM	DMF solution	129
12a		260	100	0.532	DFWM	CH_2Cl_2 solution	132
12b		360	130	0.532	DFWM	CH_2Cl_2 solution	132
12c		140	30	0.532	DFWM	CH_2Cl_2 solution	132
$(p\text{-}MeC_6H_4SO_2)_4PcH_2$			−0.50	1.34	THG	$CHCl_3$ solution	60
			−0.15	1.064	EFISH		
$(t\text{-}Bu)_4PcH_2$			−0.14	1.34	THG	$CHCl_3$ solution	60
			−0.13	1.064	EFISH		
$(OC_8H_{17})_2PcH_2$			−0.42	1.34	THG	$CHCl_3$ solution	60
			−0.13	1.064	EFISH		
2a			−0.41	1.34	THG	$CHCl_3$ solution	60
			−0.19	1.064	EFISH		
PcTiO	3.99		100	0.520	Z-scan	toluene solution	137
$(C_2H_5O)_4(C_8H_{17})_4PcTiO$	27.0		1490	0.520	Z-scan	toluene solution	137
PcVO	100			1.6	THG	OMBD film	140
DBPcVO[c]	28			1.6	THG	evaporated film	140
NcVO[b]				1.6	THG	evaporated film	140
$PcCu{-}C_{60}$			54	0.83	optical Kerr effect	toluene solution	141
PcTiO (a form)	159			2.43	THG	vacuum deposited film	158
PcTiO (amorphous)	53			1.80	THG	vacuum deposited film	158

[a] cumph, cumylphenoxy. [b] Nc, naphthalocyanine. [c] DBPc, dibenzophthalocyanine.

two-photon absorption). The occurrence of a two-photon absorption has been later confirmed by Z-scan measurements.[157] For Cu-substituted Pcs, the data suggest the existence of an additional two-photon state associated with the d−d transitions of the metal.

The importance of the macroscopic arrangement as stated above[140] has also been shown by THG measurements on a large nonlinear single crystal of vanadylphthalocyanine (VOPc) prepared on a KBr substrate by MBE.[153] The NLO response was found to be three times larger than the values obtained from previous VOPc epitaxially grown on KBr. The role of molecular interactions had been previously assessed in other related metallophthalocyanines: different polymorphs of oxotitaniumphthalocyanine (TiOPc) exhibited different $\chi^{(3)}$ values.[158] Likewise, helical assembly of the Pc cores in spin-coated films of vanadyl phthalocyanines peripherally substituted with chiral chains gives rise to enhanced third-order responses in THG experiments, as compared to the cases of the corresponding achiral derivatives.[159]

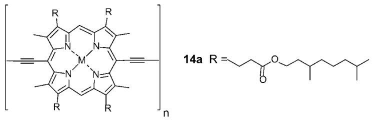
The relations between molecular configuration and NLO properties[160] of phthalocyanines have been recently demonstrated.[155] Oxomolybdenumphthalocyanine and tin phthalocyanine with a pyramidal molecular shape have been deposited onto a substrate by a molecular beam deposition technique. Larger values than those of planar metallophthalocyanines have been observed, thus pointing out that molecular shape is an important factor determining the nonlinear optical properties.

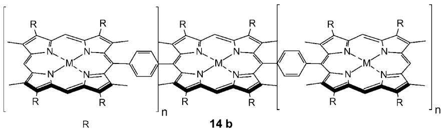
The experimental data for γ and $\chi^{(3)}$ are summarized in Table 3. It is remarkable that much higher values are measured by DFWM (up to 1.30×10^{-30} esu) and Z-scan (up to 1.49×10^{-29} esu) than by THG (4.6×10^{-32} esu). Even so, the resonance effects are expected to be larger for THG at most used wavelengths (e.g. 1.064 μm). This points out the role of nonelectronic mechanisms in DFWM and Z-scan even for picosecond pulses. Unfortunately, we are not aware of THG and DFWM (or Z-scan) measurements on the same system and under the same conditions. The best $\chi^{(3)}$ values have been obtained for OMBD or vacuum-evaporated films and reach 10^{-10} esu.

4.2. Third-Order NLO Activity in Phthalocyanine Analogues

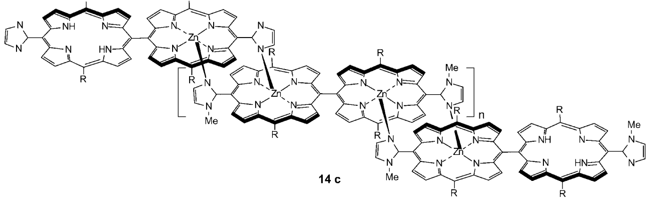
The impact of molecular design on the magnitude of the third-order nonlinear responses of porphyrins has been also widely explored. Regarding the effect of the substituents, a large improvement in the nonlinearity of porphyrins upon peripheral substitution with donor/acceptor groups has been observed.[161] Moreover, first- and second-generation dendritic tetraphenylporphyrins have been prepared and measured using the Z-scan technique.[162] The results show that the second-generation dendritic porphyrin has a larger γ value than the first-generation counterpart. Since the increase in the second-order molecular hyperpolarizability cannot be explained on the basis of inductive and resonance effects, the increasing electron-rich microenvironment created by the dendritic branches can rationalize the observed trend.

The effect of the metallic ions and axial ligands on the molecular hyperpolarizability of porphyrins has been investigated. Z-scan experiments over different transition metal complexes exhibit a significant increase for divalent ions with decreasing d-shell occupancy.[163] In the case of tetravalent metal centers, a dramatic enhancement of the nonlinear parameter was found for electronegative axial ligands, for example, iodine.





14 b



14 c

Very large electronic nonlinearity results from a highly conjugated porphyrin polymer **14a,** when measured by DFWM at 1.064 nm with 45 ps pulses.[164] Even though the polymer is weakly absorbing at this wavelength, the resonant absorption should be insignificant within that time scale. As for phthalocyanines, the extension of the conjugated π-system renders an enhancement of the microscopic second-order hyperpolarizability. The γ value per macrocycle in **14a** is by 3 orders of magnitude higher than that of the monomer. This polymer and a related analogue bearing ethynylaryl substituents, which extend the conjugation of the porphyrin perpendicularly to the main chain,[165] possess one of the largest nonlinearities of any conjugated organic polymer studied to date. Very recently, double strand ladder complexes based on polymers related to **14a** have been studied by means of the DFWM technique.[166] In these polymers the two chains are held together through coordination of the zinc(II) centers with 4,4′-bipiridyl ligands. The authors observed an amplification of the optical nonlinearity with regard to the single strand polymer, due to an increased conjugation as a consequence of the forced intrachain planarization. A series of related oligomers, which consist of porphyrins bridged by 1,4-phenylene moieties through their *meso* positions (**14b**), had been previously studied using the Z-scan technique.[167] In this case, the real part of $\chi^{(3)}$ increased linearly with the number of monomer units, so that the value per monomer unit was almost constant. Enhancement in the third-order nonlinear susceptibilities due to $\pi-\pi$ electronic couplings between porphyrin macrocycles had also been pointed out previously in face-to-face stacked dimers.[168] Two series of self-assembled porphyrin wires, one being terminated by a Zn(II) porphyrin and the other by a free-base porphyrin, have been measured by the time-resolved optical Kerr effect. The building blocks consist of porphyrin units linked directly at the *meso*−*meso* positions (**14c**); these dimers bear imidazolyl moieties capable of coordinating to a Zn(II) porphyrin core of another different building block. The hyperpolarizability values found are extremely large, because of the large molecular polarization in this type of array.[169]

Another interesting structure−property relationship is the dependence of the third-order response on the molecular shape. For instance, basket handle porphyrins have shown reduced susceptibility values[170] with regard to other porphyrin systems, probably because the deformation from a planar structure hinders the delocalization of the π-electrons of the molecule.

To gain more insight into the factors affecting the third-order properties, asymmetric penta-azadentate porphyrin-like metal complexes **15** have been synthesized and their third-order molecular parameters measured by means of DFWM experiments in solution.[171] This type of 22-π-electron systems allows a variety of metal-to-ligand and ligand-to-metal charge-transfer states and shows very large γ values, thus indicating that a tailored change in the structure of the core of either phthalocyanines or porphyrins can be one of the most effective tools to modulate and improve the nonlinear response. It has been observed that the γ values of these complexes are highly dependent on the nature of the R group (in **15**), increasing as the number of conjugated π-electrons increases. As expected, the more delocalized π-electron system has the largest γ value. On the other

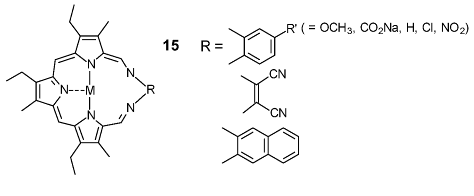


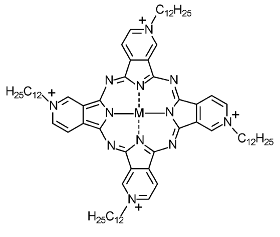
Table 4. Third-Order Nonlinear Parameters for Selected Phthalocyanine Analogues

compd	$\chi^{(3)}$ ($\times 10^{-14}$ esu)	γ ($\times 10^{-32}$ esu)	λ (μm)	technique	condensed phase/ solution	ref
$TPPH_2$[a]		−850	0.784	Z-scan	toluene solution	161
(o-$C_2H_5OOCCH_2OC_6H_4)_4PorH_2$[b]		−4820	0.784	Z-scan	toluene solution	161
(p-$C_2H_5OOCCH_2OC_6H_4)_4PorH_2$[b]		−670	0.784	Z-scan	toluene solution	161
TPPZn[a]		1002	0.802	Z-scan	toluene solution	162
TPPCu[a]		1660	0.802	Z-scan	toluene solution	162
TPPNi[a]		2670	0.802	Z-scan	toluene solution	162
$TPPH_2$[a]		5280	0.802	Z-scan	toluene solution	162
$R_4TPPSnI_2$[a]		10970	0.802	Z-scan	toluene solution	162
$R_4TPPSnBr_2$[a]		970	0.802	Z-scan	toluene solution	162
14a	2.9×10^{-17} $m^2 \cdot V^{-2}$		1.064	DFWM	spin-coated film	164
14b ($n = 1$)		−38	0.640	Z-scan	CH_2Cl_2 solution	167
14b ($n = 2$)		−61	0.640	Z-scan	CH_2Cl_2 solution	167
14b ($n = 3$)		−71	0.640	Z-scan	CH_2Cl_2 solution	167
14c ($n = 0$)		180[c]	0.800	optical Kerr effect	$CHCl_3$ solution	169
14c ($n = 1$)		950[c]	0.800	optical Kerr effect	$CHCl_3$ solution	169
14c ($n = 3$)		1300[c]	0.800	optical Kerr effect	$CHCl_3$ solution	169
BHTPPCu[d]	103		0.532	DFWM	CH_2Cl_2 solution	170
15a ($R' = NO_2$)		75	0.532	DFWM	MeOH solution	171
15b		120	0.532	DFWM	MeOH solution	171
15c		34	0.532	DFWM	MeOH solution	171
(p-$C_2H_5OOCCH_2OC_6H_4)_4$chlorin		−1550	0.784	Z-scan	toluene solution	172
ThpCu[e]		−0.11	1.340	THG	$CHCl_3$ solution	176
		−0.10	1.940	THG	$CHCl_3$ solution	
ThpNi[e]		−0.15	1.340	THG	$CHCl_3$ solution	176
		−0.50	1.940	THG	$CHCl_3$ solution	
ThpCo[e]		−0.61	1.340	THG	$CHCl_3$ solution	174
		−1.10	1.940	THG	$CHCl_3$ solution	
16 (M = Cu) (low-aggregated)	8.8		1.064	THG	spin-coated film	177
16 (M = Cu) (high-aggregated)	36		1.064	THG		
16 (M = Ni) (low-aggregated)	6.2		1.064	THG	spin-coated film	177
16 (M = Ni) (high-aggregated)	19.2		1.064	THG		
16 (M = Co) (low-aggregated)	12.1		1.064	THG	spin-coated film	177
16 (M = Co) (high-aggregated)	74		1.064	THG		

[a] TPP, tetraphenylporphyrin. [b] Por, porphyrin ring. [c] $|\gamma_{yyyy}|$. [d] BHTPP, basket handle tetraphenylporphyrin. [e] Thp, triazolehemiporphyrazine.

hand, a linear correlation between the γ values of the complexes and the Hammet parameters of the R′ groups (in **15**) was found. Variation in the metal center also has a significant effect on the hyperpolarizability values. Porphyrin analogues such as tetraphenylchlorin derivatives have also been measured by the Z-scan technique.[172] The authors find enhancements in the hyperpolarizability values of these compounds in comparison to similarly substituted porphyrins.[161]

Third-order experiments have also been performed on other Pc-related compounds, such as subphthalocyanines,[173,174] triazolehemiporphyrazines,[175,176] and tetrapyridinoporphyrazines.[177] Sublimated chloroboron subphthalocyanine thin films[174] have been investigated via THG in the range 950−2000 nm, and the $\chi^{(3)}$ values obtained are larger than those obtained for phthalocyanines in the same frequency range.[144] Other authors have explored the third-order NLO properties of solutions of bromoboron(trineopentoxy)-subphthalocyanine using DFWM.[173] The measured $\chi^{(3)}$ value is 2 orders of magnitude higher than that found for chloroboronsubphthalocyanine thin films,[174] but in this case, the value is resonantly enhanced.[173] Triazolehemiporphyrazines are macrocycles composed of two isoindole units and two triazole ones bridged through aza functions. An enhancement of the third-order response with unfilled d-shell metal substitution was demonstrated,[176] as in phthalocyanines.[121] PMMA spin-coated and Langmuir−Blodgett films of a series of 3,4-tetrapyridinoporphyrazines **16** were tested for their THG response.[177] The study on spin-coated films showed clear evidences of the role of molecular aggregation in enhancing the THG yield.



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The measured γ and $\chi^{(3)}$ values for a number of porphyrins and Pc-related systems are summarized in Table 4. As for Pcs, one first notices that the data obtained with DFWM or Z-scan are orders of magnitude higher than those obtained with THG or EFISH. The highest value obtained by Z-scan on R_4-$TPPSnI_2$ reached 10^{-28} esu. This behavior should be associated with the dominant role of nonparametric processes mostly caused by optical pumping of electronic levels (see section on Optical Limiting Behavior). The THG values exclusively associated with electronic processes are of the order of 10^{-32} esu, somewhat smaller than the best values reported for Pcs.

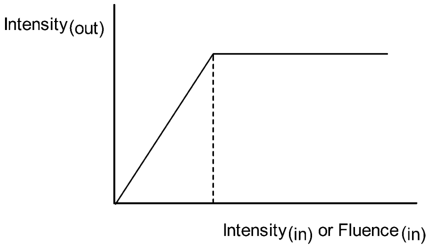


Figure 3. Ideal behavior of an optical limiter.

5. Optical Limiting Behavior

Optical limiting (OL) is a nonlinear effect consisting of a decrease in the transmittance of the NLO material under high-intensity illumination. Thus, the transmission of an optical limiter is high at normal light intensities and low for intense beams. Ideally, the output energy of a limiter rises linearly with input until a threshold is reached, as shown in Figure 3. After the threshold, the output energy is clamped at a given value for any larger input intensity. Among the different functions such devices can perform, the most useful one is the protection of optical elements and sensors against damage by exposure to sudden high-intensity light.

The main mechanisms to achieve optical limiting are nonlinear absorption (NLA) and nonlinear refraction (NLR), but other effects such as nonlinear scattering can also contribute to the limiting. Materials with a positive nonlinear absorption coefficient, that is, that exhibit *reverse saturable absorption* (RSA), cause a decrease in transmittance at high-intensity levels and so operate as optical limiters. Two-photon absorption (TPA), described by the imaginary part of the third-order susceptibility $\chi^{(3)}(\omega;\omega,-\omega,\omega)$, may account for OL, but excited-state absorption (ESA), which refers to a sequential two-photon absorption, constitutes the fundamental mechanism for RSA and OL in phthalocyanines. On the other hand, nonlinear refraction means that the refractive index of a material varies under the influence of the incident light. This index variation forms a lens that can defocus the beam and deflects a fraction of the light into the wings of the beam, where it is blocked by a properly located aperture. Therefore, optical limiting is not directly caused by nonlinear refraction unless some geometrical arrangement is used to limit the beam. Nonlinear refraction is determined by the real component of $\chi^{(3)}(\omega;\omega,-\omega,\omega)$. As for nonlinear scattering, this mechanism can contribute to OL because an increasing fraction of the pulse energy is scattered away as input fluence is increased.

As mentioned above, the most efficient mechanism to achieve OL is the sequential two-photon absorption, which involves the nonparametric optical pumping of low-lying electronic states of the material.[178] Typically, this kind of nonlinearity is larger than that arising from the third-order susceptibility but the response time is generally slower. The theoretical analysis is not based on the susceptibility approach but on rate-equation formalisms describing the filling and relaxation of the involved electronic levels through sequential one-photon transitions. A five-level diagram (Figure 4) can be used to discuss the nonlinear absorption of phthalocyanines.

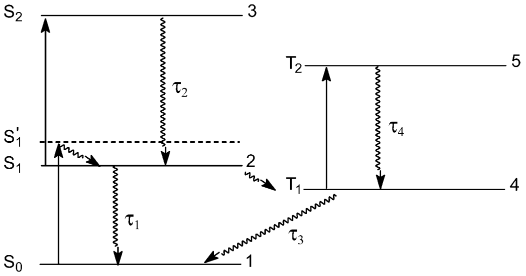


Figure 4. Five-level energy diagram accounting for the nonlinear absorption behavior of phthalocyanines and related compounds.

S and T are singlet and triplet states, respectively, in Figure 4. Under illumination, an initial photon 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. This state decays into either S_0 or a lower energy triplet state T_1 through a spin-flipping process (assisted by spin−orbit coupling). The molecule in that triplet state may absorb another photon and be excited to a higher triplet level T_2. Moreover, one-photon transitions from S_1 to a higher lying singlet state S_2 are also possible. If the material has an excited-state (S_1 or T_1) absorption cross section (either $\sigma_{ex,S}$ or $\sigma_{ex,T}$) larger than the ground-state cross section (σ_0) and if the incident beam induces a significant population in the excited states, the effective absorption coefficient of the material increases and *reverse saturable absorption* occurs. To achieve a strong nonlinear absorption, both a large excited-state absorption cross section and a long excited-state lifetime are required. In many materials, two situations may occur. If the lifetime of the S_1 excited state is longer than the pulse width, singlet−singlet absorption may take place before a significant population of the triplet T_1 state has developed. Under these conditions, the simplest three-level model (S_0, S_1, and S_2) can be used to discuss the results and $\sigma_{ex,S}/\sigma_0$ is the relevant ratio for optical limiting behavior. Values higher than 10 have been obtained.[179] On the other hand, processes occurring under long pulse illumination or with molecules presenting high intersystem crossing rates give rise to a significant population of the T_1 level and so to triplet−triplet T_1−T_2 transitions. The last situation is preferable, since the absorption cross section of the S_1−S_2 transition is usually smaller than that of the T_1−T_2 transition (at least for phthalocyanines). In fact, the ratio $\sigma_{ex,T}/\sigma_0$ reaches values higher than 30.[180] Moreover, when the lifetime of the excited state being pumped is longer than the pulse width of the incident light, the changes in the absorbance are fluence ($J\cdot cm^{-2}$), not intensity ($W\cdot cm^{-2}$), dependent. Limiting the fluence is desirable, since damage to optical devices used to be fluence dependent.

Thus, the ratio of cross sections σ_{ex}/σ_0 can be used to evaluate RSA materials. That means that a large excited-state absorption cross section is not the only requirement, but also a large difference between the ground- and excited-state cross sections. Other criteria that a material should fulfill to be considered

Table 5. Optical Limiting Performance Parameters for Selected Phthalocyanines

compd	β (cm·GW^{-1})	σ_e^{eff} ($\times 10^{-18}$ cm^2)	σ_e/σ_g	**Fs** (J·cm^{-2})	λ (μm)	technique	condensed phase/ solution	ref
PcAlCl		18			0.532	Z-scan (ps)	methanol solution	179
$(t\text{-Bu})_4\text{PcInCl}$			30	0.47	0.532	nonlinear transmission (ns)	toluene solution	180
$(\text{OCH}_2\text{CF}_3)_8\text{PcVO}$			34	1.1	0.532	nonlinear transmission (ns)	toluene solution	180
$(t\text{-Bu})_4\text{PcGaCl}$			13.5			Z-scan (ns)	toluene solution	195
$(t\text{-Bu})_4\text{PcInCl}$			27.5			Z-scan (ns)	toluene solution	195
$[(t\text{-Bu})_4\text{Pc}]_2\text{GaO}$			11.3			Z-scan (ns)	toluene solution	195
$[(t\text{-Bu})_4\text{Pc}]_2\text{InO}$			12.4			Z-scan (ns)	toluene solution	195
$[(t\text{-Bu})_4\text{Pc}]_2\text{In}_2$			12.5			Z-scan (ns)	toluene solution	196
18		120			0.550	nonlinear transmission (ns) and Z-scan	toluene solution	191,192
$(t\text{-Bu})_4\text{NcGa}(p\text{-trifluoromethyl})$			9.2	8.5	0.532	Z-scan (ns)	toluene solution	210
$(t\text{-Bu})_4$PcCo-≡-≡-CoPc$(t\text{-Bu})_4$	35		11	9.5	0.532	Z-scan (ns)	toluene solution	211
$(\text{C}_8\text{H}_{17})_2\text{NCOCH}_2\text{OPcH}_2$	0.04				1.064	Z-scan (ps)	CHCl_3 solution	157
$(\text{C}_8\text{H}_{17})_2\text{NCOCH}_2\text{OPcCu}$		1.4			1.064	Z-scan (ps)	CHCl_3 solution	157
$(\text{OC}_{10}\text{H}_{21})_8\text{PcPd}$		75			0.532	nonlinear transmission (ns)	CHCl_3 solution	214
$(\text{OC}_{10}\text{H}_{21})_8\text{PcNi}$		55			0.532	nonlinear transmission (ns)	CHCl_3 solution	214
$(\text{OC}_{10}\text{H}_{21})_8\text{PcCo}$		90			0.532	nonlinear transmission (ns)	CHCl_3 solution	214
$(\text{OC}_{10}\text{H}_{21})_8\text{PcCu}$		72			0.532	nonlinear transmission (ns)	CHCl_3 solution	214
$(\text{OC}_{12}\text{H}_{25})_8\text{PcPb}$		60[a] 7[b]	19.4[c]		0.532	nonlinear transmission (ns)	toluene solution	217
(*R*)-TMBOPcCu[d]		35	5		0.532	nonlinear transmission (ns) and Z-scan	CHCl_3 solution	223

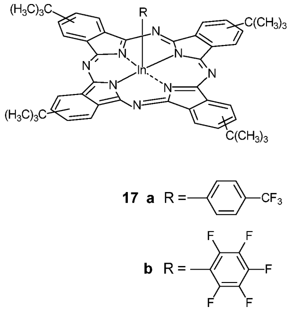
[a] Cross section for the triplet state. [b] Cross section for the singlet state. [c] Cross section ratio for the triplet state. [d] TMBO, tetrakis(2-methoxy-1,1′-binaphthalen-2′-oxy).

an useful optical limiter include broad spectral bandwidth for limiting, fast response times (in the subnanosecond regime), low threshold for the nonlinear response (the maximum permissible exposure for human eyes to nanosecond pulses in the visible is less than 0.2 μJ), and a high threshold for damage. Hence, other authors have referred to the threshold fluence as the best parameter to quantify and compare the efficacy of optical limiting materials. This can be defined as that fluence at which the transmission drops to half of its linear value. The saturation fluence has also been used to quantify the optical limiting response. Despite the use of these fluence parameters, the ratio between the excited-state absorption cross section and that of the ground state has been widely accepted as an indicator of limiting power, even if the use of this parameter can be misleading in some cases, since it overemphasizes the advantage of reducing σ_0 to achieve a large figure of merit.[19] Thus, for example, σ_{ex}/σ_0 can be quite high for a material which exhibits a weak nonlinear response in terms of transmission versus pulse-energy density. For this reason, it has also been suggested that the cross section difference ($\sigma_{ex} - \sigma_0$) could be a more useful indicator of limiting action.[181] It is difficult to define how to quantify the magnitude of the optical limiting action, since it depends on the different mechanisms involved, the techniques employed, and the different opinions of the authors. Anyhow, one should be especially careful in comparing the parameters obtained for compounds that have been measured under different conditions.

A variety of organic and organometallic materials have been shown to present positive nonlinear absorption coefficients in the visible, namely fullerenes[182] and phthalocyanines.[17,183,184] Phthalocyanines are very promising materials for optical limiting in the visible and NIR spectral range, because of their appropriate photophysical properties. These macrocycles show high transmission between the Soret and Q bands and exhibit strong excited-state absorption, high triplet yields, and long excited-state lifetimes. Varying the peripheral substitution and central metal cation, one can control ground-state and excited-state spectra and lifetimes. Moreover, the spectral bandwidth or window over which the limiter operates can also be engineered by altering both the main ring and the peripheral substituents, thus allowing a fine-tuning of the performance parameters. For these reasons, phthalocyanine derivatives have received a great deal of attention as reverse saturable absorbers and much work has been devoted to understand the mechanisms involved in the limiting response of these macrocycles.[185,186]

5.1. Optical Limiting in Phthalocyanines

Optical limiting with phthalocyanines[187] was first reported in 1989 for chloroaluminumphthalocyanine (CAP).[188] This compound happened to be a relatively good optical limiter, showing reverse saturable absorption in methanol solution. Using the Z-scan technique with picosecond pulses at 532 nm, it was established that excited-state absorption from the singlet state was the dominant nonlinear absorption in this type of compounds,[179] as for the silicon(IV) naphthalocyanine derivative which exhibited even larger nonlinear absorption coefficients than the ClAlPc. The absorption cross section values were, then, calculated for these materials (Table 5). However, the optical performance of this phthalocyanine material was shortly beaten by the Pb(II) tetrakis(β-cumylphenoxy)phthalocyanine.[189] It is remarkable that all these materials showed a large contribution of the nonlinear refraction to the limiting. From then on, much research work has been devoted to the development of new phthalocyanines with improved optical limiting capabilities. For example, it has been demonstrated that the insertion of heavy atoms into the phthalocyanine ring causes significant effects on RSA and optical limiting performance for nanosecond laser pulses,[190] since they increase the intersystem crossing rate from S_1 to T_1. Nanosecond nonlinear transmission experiments at 532 nm on MPcs (M = Al, Ga, In, Tl, Si, Ge, Sn, Pb) show cross section ratios ranging from 10 to 16 for group IIIA and from 10 to 18 for group IVA, as the metal becomes heavier. Indium leads to an even faster intercrossing rate than lead, despite its lower atomic number, and so improves the limiting threshold.[180] In fact, both Pb(II) tetrakis(β-cumylphenoxy)phthalocyanine[189] and In(III) tetrakis(*tert*-butyl)phthalocyanine chloride[180] have been used to construct optical limiters that fulfill the requirements for a practical device. Particularly, InClPc(*tert*-butyl)$_4$ shows an increase of the nonlinear attenuation at high energies by a factor of 3 compared to AlClPc. Very recently, Shirk, Hanack, and co-workers have described the optical limiting properties of new highly soluble axially substituted indium phthalocyanines **17**.[180,191,192] The introduction of axial aryl substituents has a positive effect in suppressing the aggregation of the macrocycles in solution, which has been shown to alter the excited-state relaxation time and, so, the effective nonlinear absorption of the material. The nanosecond nonlinear absorption and the optical limiting of these phthalocyanines are shown to be dominated by a strong triplet state absorption, and the excited cross section is larger than that of the parent InClPc(*tert*-butyl)$_4$. However, these indium phthalocyanines show lower σ_{exc}/σ_0 ratios, which indicates that, in this case, the cross section ratio is not representative of the strength of the nonlinear absorption. The refractive contribution to the limiting is small because the electronic and thermal contributions are opposite in sign. An optical limiter using the *p*-(trifluoromethyl)phenylindium(III) tetra-*tert*-butylphthalocyanine **17a** exhibits a lower threshold for optical limiting and a lower transmission at high fluences than the previously reported indium(III) phthalocyanine chloride. These results suggest that the variation of the axial substituents in indium phthalocyanines can be an efficient tool for optimizing the structural characteristics and optical limiting performances of this kind of materials. For instance, aceylacetonate ligand has been axially appended to the central indium metal and preliminary Z-scan meaurements show it promising for achieving good OL performances.[193] The same authors have also prepared axially bridged μ-oxo dimers of gallium(III)[194,195] and indium(III)[195] phthalocyanines peripherally substituted with *tert*-butyl groups. Z-scan measurements at 532 nm show higher Im $\chi^{(3)}$ and γ values for the dimers than for the monomeric related compounds axially substituted with a chlorine atom. However, tetrakis(*tert*-butyl)phthalocyanineIn(III) chloride is the molecule with the larger κ (σ_{exc}/σ_0) value of the series. These authors have also carried out preliminary Z-scan studies over solutions of a novel axially bridged indium phthalocyanine dimer with an In–In bond.[196] This dimer exhibits a lower cross section ratio than the monomeric InClPc(*tert*-butyl)$_4$ but a similar one to that reported for the corresponding μ-oxo dimer.

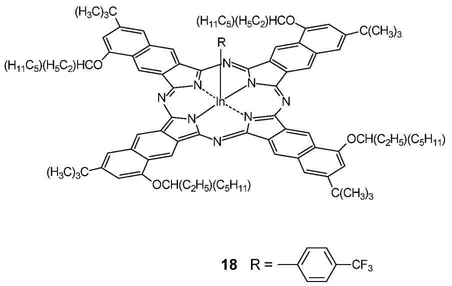


Other metallic phthalocyanines that have recently shown good OL performances are the paramagnetic VOPc derivatives.[180,197] It appears that the magnetic moments contribute to the spin–orbit coupling and enhance the intercrossing rate. Even though some VOPc derivatives show larger σ_{ex}/σ_0 values than the InClPc(*tert*-butyl)$_4$,[180] the fluence saturation of the former is also larger, which means that less excited-state populations are produced. Rare-earth phthalocyanines are novel candidates for optical limiting processes, since they have recently exhibited high excited-state absorption cross sections.[197–204] For example, Eu(IV) and Gd(IV) sandwhich-type derivatives have been recently measured via fluence-dependent transmittance measurements.[201] The EuPc$_2$ exhibits better optical limiting performance probably due to its bigger radius that weakens intramolecular $\pi-\pi^*$ interaction and, so, increases triplet-state lifetimes. Other authors have studied a series of rare-earth phthalocyanines (i.e. Nd, Eu, Sm, La) in DMF solution.[202] SmH(Pc)$_2$ yields the maximum cross section value of the series for an excited-state absorption mechanism. In addition, the wavelength dependence of the nonlinear absorption of sandwich-type bisphthalocyanines (SmH(Pc)$_2$, Eu(Pc)$_2$, Nd(Pc)$_2$) has been addressed. [203,204] Both Eu(IV) and Nd(IV) complexes can be used as reverse saturable absorbers up to 604 nm, but SmH(Pc)$_2$ behaves as a saturable absorber at this wavelength.[204] Another remarkable heavy atom effect is that observed in solutions of a phthalocyanine pentamer in a chloroform/methyl iodide solution.[205] Compared with the case of chloroform, the Pc-based derivative dissolved in this mixture of solvents shows better OL performance at the same linear transmittance. An explanation based on the external heavy atom effect is proposed.

Blau and co-workers have experimentally measured some series of structurally different phthalocyanine derivatives containing Zn(II), Co(II), Ni(II), Pd(II), Pb(II), Ga(III), and In(III) by means of the Z-scan technique.[206] It was found that the introduction of nickel or cobalt into the phthalocyanine cavity produced a strong reduction of the magnitude of the nonlinear absorption as compared to the cases of the other metallic phthalocyanines. Among all the derivatives measured in this work, the InClPc(*tert*-butyl)$_4$ compound exhibited the largest ratio of excited- to ground-state absorption cross section, while the palladium(II) derivative was the compound with the largest nonlinear absorption coefficient.[207]

Some applications require materials that display high transmission in the red region of the spectrum. Naphthalocyanines have their Q band shifted to the IR with respect to the one of phthalocyanines as a consequence of their extended π-electron system.

Therefore, they have a transmission window in the red and yellow region of the spectrum, so that they provide alternative materials for OL when one wishes to use them in environments in which it is necessary to see red lights or displays. Some substituted naphthalocyanines have been shown to be very promising materials for practical OL devices.[208,209] In(III) naphthalocyanines[191,192] **18** bearing both *tert*-butyl and ethylhexyloxy moieties, specially designed to resist aggregation, have shown large excited-state cross sections and lifetimes. As their phthalocyanine homologues, Ga(III) naphthalocyanines are also interesting materials for optical limiting.[210] Moreover, the determination of the influence of the electronic interactions between macrocycles on the nonlinear absorption of Pc-based systems is also an appealing task. Highly conjugated ethynyl- and butadyinyl-bridged bis(phthalocyanines) containing Zn(II) and Co(II) cations, such as **19**, have shown moderate cross section ratios,[211] but ones higher than those of the model monomeric phthalocyanines, particularly for the cobalt(II) derivatives. The inclusion of heavy metal atoms in this type of structures could render very efficient OL materials.



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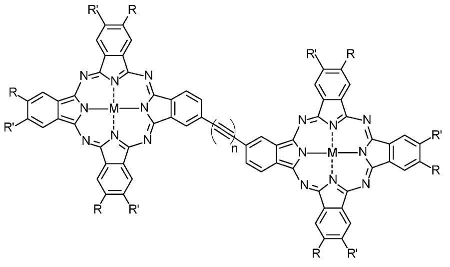
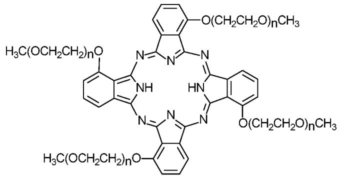


19 n = 1,2
M = Zn, Co

Another molecular engineering approach that has been used to tune the spectral range of the limiter is the introduction of alkoxy substituents into the α-positions of both phthalocyanines and naphthalocyanines. Particularly, indium and lead octabutoxynaphthalocyanines with a red-shifted OL response have been measured.[212] Generally, the main restricting factor for the processing and application of phthalocyanines as optical limiters is their rather low solubility in common organic solvents. Moreover, proper saturation fluence requires a high concentration of the chromophore in the optical beam. These requisites have prompted the study of the OL behavior of highly soluble phthalocyanines.[157,213−218] A very interesting issue is the effect of electron-donor[214,215,217] and electron-acceptor[219−221] groups on the OL performance of peripherally substituted phthalocyanines, since these peripheral substituents are expected to influence the dipole moments of the involved optical transitions. It appears that strong donor peripheral alkoxy substituents improve the OL response, with low OL threshold and clamped fluences.[214,215,217] Likewise, an enhanced OL response associated with strong electron-withdrawing moieties has been found in Z-scan experiments for hexadecafluorophthalocyanines containing Ti(IV), V(IV), Zr(III), and In (III)[219] and for Ti(IV) tetra(trifluoromethyl)phthalocyanine,[219,220] as compared to the cases of the corresponding phthalocyanines bearing weak electron-releasing groups (i.e. *tert*-butyl). Following the effect of peripheral substituents, some authors have been dealing with the preparation of phthalocyanines bearing optically active moieties. Specifically, a phthalocyanine containing binaphthyl moieties has been prepared and it has been shown that (*S*)- and (*R*)-optical isomers present similar optical limiting behavior.[222,223] These chromophores are potential materials for RSA and also present a large defocusing effect which may be helpful in further enhancing the OL performance. OL behavior has also been studied in octacarboxyphthalocyanine.[224] This type of peripheral substitution provides water solubility, which can be of interest in environmental protection and green chemistry.

The combination of two different active moieties in a unique chemical structure can lead to improved OL performances. A fullerene−phthalocyanine dyad has been prepared and studied for its OL properties.[225] The results show that both components behave as isolated systems that independently contribute to the reverse saturable absorption.

The attachment of appropriate lipophilic substituents can give rise to high-quality solid films, as demonstrated by Shirk and co-workers. For example, the introduction of amine-epoxy-type chains at the periphery of the phthalocyanine core affords clear transparent films, which have been measured for their OL capability.[226] With the aim of obtaining liquid phthalocyanines at room temperature, which could behave as reverse saturable absorbers,[227] ethylene oxide[228,229] and poly(dimethylsiloxane)[230−232] oligomers have been attached to the Pc core. Particularly, the introduction of poly(ethylene oxide) chains (**20**) has been successful in generating optically clear intrinsically liquid phthalocyanines having large nonlinear absorption perfomances.[216,229] For example, metal-free poly(dimethylsiloxane)phthalocyanine is a viscous liquid that possesses excellent film forming properties and has an excited-state cross section larger than that of the ground state.[231] However, this compound exhibits a short excited-



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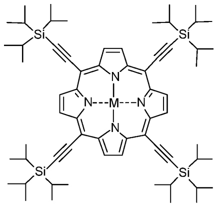
state lifetime that can be attributed to the strong aggregation of the molecules, which could be avoided through metal substitution. Thus, lead(II) poly(dimethylsiloxane)phthalocyanine has been also synthesized.[230,233] Optical limiting measurements reveal that the excited-state cross section of this compound is similar to the ratio reported for Pb(II) tetrakis(cumylphenoxyphthalocyanine). Other sol−gel materials,[234−238] guest−host systems,[239−241] thin films,[242,243] and nanoparticle dispersions[244] containing different Pc chromophores have also been investigated. For example, thin films of Pb(II) tetrakis(cumylphenoxyphthalocyanine) have been produced by forming highly concentrated solutions of the dye in polymeric hosts.[245] In this particular case, the single layered films exhibited nonlinear absorption coefficients larger than those observed with solutions of the corresponding phthalocyanine. Nonlinear refraction has been investigated on evaporated thin films of a tin phthalocyanine by means of DFWM and Z-scan techniques.[246] One should note that, as mentioned above, the response time of the nonlinear absorption and refraction in thin films of phthalocyanine materials is strongly affected by intermolecular interactions.[247]

Relevant perfomance parameters for a number of Pc systems are listed in Table 5. The data are scarce and fragmentary. Cross sections $\sigma_e = 120 \times 10^{-18}$ cm^2 have been measured, and values of σ_e/σ_g up to 30 have been achieved.

5.2. Optical Limiting in Phthalocyanine Analogues

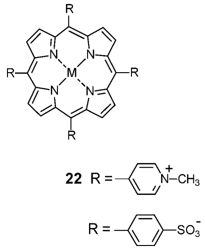
Porphyrins are also effective optical limiters, since they can exhibit strong excited-state absorption, high triplet yields, and long excited-state lifetimes. As for phthalocyanines, the ground-state absorption of porphyrins is confined to the Q and B bands, exhibiting high transmission in the spectral window between these two main absorptions. Control of the excited-states lifetimes and cross sections can be indeed achieved by varying the peripheral substitution, the extension of the π-conjugation, and the central atom. Therefore, the ease of these structural modifications makes them very interesting targets for studying the factors affecting the OL behavior.

Pioneer studies on porphyrins were undertaken by Blau et al. on metal-free and metallic *meso*-tetraphenylporphyrins (TPPs).[248] Many studies on these systems have been devoted to infer the effect of substitution on the factors affecting the OL response. For example, a series of metallic octabrominated tetraphenylporphyrins[249] have shown nonlinear absorption which happened to be extremely large for the Zn(II) derivative and even larger than that found for the Pb(II) homologues. It had already been reported that the introduction of bromine atoms at the pyrrolic positions increases drastically the intersystem crossing rate.[250] Some authors have measured the reverse saturable absorption behavior of *meso*-tetraalkynylporphyrins.[251−256] Particularly, a systematic survey of the group III and IV metal complexes of porphyrin **21** has been reported recently.[256] The authors found an increase in the σ_{ex}/σ_0 when moving toward the heavier members of each group. Thus, the In(III), Tl(III), and Pb(II) complexes show the highest cross section ratio for macrocyclic dyes; this fact indicates that the heavy atom effect is again one of the most significant factors influencing limiting behavior. More recently, the nonlinear optical transmission of *meso*-tetrakis{4-[2-(trimethylsilyl)ethynyl]-phenyl}porphyrins (Zn(II), Ni(II), Ga(III), In(III), and Sn(IV) complexes) has been determined.[257] The amount of excited-state absorption is increased with regard to the cases of previously reported TPPs[248] by modifications at the *para* positions of *meso*-phenyl rings.



21 **a** M = GaCl
b M = InCl
c M = TlCl
d M = SnCl$_2$
e M = Pb

The nonlinear refractive index and nonlinear absorption coefficient have been inferred from Z-scan experiments performed over negatively and positively charged *meso*-substituted porphyrins **22**.[258,259] The authors point out a strong reorientational contribution to the nonlinear response for the metallic complexes, and the values of the nonlinear absorption coefficients are very small. They are slightly higher for the free bases where nonlinear refraction is negligible. Tetratolyl-substituted porphyrins also exhibit nonlinear absorption at both 532 and 600 nm.[260] The heavy atom effect in tetratolylporphyrinatophosphorus(V) dichloride[261] has been found to lower the limiting threshold with regard to the free-base derivative, since this metallic derivative exhibits faster ISC, leading to larger excited-state absorption from T_1. Moreover, the introduction of charge-transfer (CT) states through axial substitution of the phosphorus atoms with azoarene moieties enhances the nonlinear absorption and optical limiting threshold.[262]



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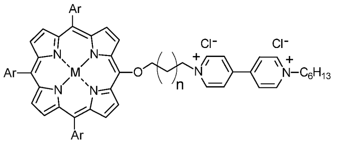
Large optical limiting responses can also be obtained from porphyrin-based dyads, which display charge-transfer processes. For example, porphyrin−viologen systems **23**[263] turned out to be more efficient optical limiters at 600 nm than both the monomeric model derivative and a solution of porphyrin with added viologen[264] studied by means of nanosecond nonlinear transmission measurements. From these results, one can conclude that photoinduced electron transfer can originate more optical limiting than



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excited-state absorption. This approach may lead in the future to very large OL performances, since, in addition to the typical factors modulating the NLO response, such as metal and peripheral substitution, these binary systems allow the tuning of the optical limiting by changing the length and the nature of the spacer, which therefore may affect the amount of the transient absorption. The same authors have also measured nonlinear transmission at several wavelengths of porphyrin−tetraviologen arrays, which also show reverse saturable absorption by means of photoinduced intramolecular electron transfer.[265] Other interesting dyads with the predicted large excited-state absorption cross section in their charge-separated state are those comprising both a porphyrin and fullerene moieties. Specifically, a donor−acceptor system composed of a porphyrin and a fullerene linked through an *o*-phenylene bridge has been prepared and measured for its optical limiting ability.[266,267] However, the OL performance of the dyad is poorer than that of the model compounds, probably due to the ultrashort lifetime of the charge-separated species. Nevertheless, interesting structure−activity relationships related to the electron-donating abilities of the *meso* substituent on the porphyrin moiety have been found. Another two-component system reported recently is an axially linked porphyrin−osmium cluster complex,[268] prepared by reaction of azido(tetra-*p*-tolylporphyrinato)indium(III) (TPPInN$_3$) with the osmium cluster [Os$_3$(μ-H)$_2$(CO)$_{10}$]. This complex exhibits a larger figure of merit κ than the starting TPPInN$_3$ (see Table 6).

The nonlinear absorption properties of benzoporphyrins have also been investigated. The first studies reported that excited-state absorption is the dominant factor for the nonlinear optical behavior of these derivatives.[269] This assessment has lately been confirmed by other authors who have studied a series of metallo *meso*-tetraaryltetrabenzoporphyrins.[270] Similar results have been obtained with *meso*-tetrathienyltetrabenzoporphyrins.[271] In regard to extended π-conjugated systems, the optical limiting properties of the porphyrin polymer **14a** have been reported.[272] Experiments performed at 532 nm revealed a strong decrease in laser light transmission with increasing excitation intensity, but the calculated figure of merit is lower than that of the monomer model compound, owing to its higher linear transmittance at the excitation wavelength. Supramolecular arrangements of butadiyne-linked bisporphyrins show two-photon and three-photon absorption when measured by Z-scan at wavelengths from 817 to 1282 nm with a femtosecond pulse laser.[273]

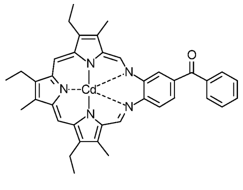
As mentioned above, pentaazadentate porphyrin-like metal complexes are efficient NLO materials. Optical limiting based on reverse saturable absorption can also be alterated by introducing either different substituents onto the benzene rings or different metal ions into the macrocyclic ligand.[274,275] Particularly, the strong reverse saturable absorption shown by compound **24**[276] makes these kinds of analogues potential candidates for optical limiting of nanosecond pulses.

Substituted tetraazaporphyrins have also been studied for their OL properties.[277,278] Two-photon absorption of a series of octasubstituted derivatives **25** has been measured in the excitation region close to the Q band.[277] Strong resonance enhancement of the TPA efficiency has been found. It is also remarkable that the absolute value of the TPA is dramatically enhanced by strong electron-accepting substi-

Table 6. Optical Limiting Performance Parameters for Selected Phthalocyanine Analogues

compd	β (cm·GW^{-1})	σ_e^{eff} ($\times 10^{-18}$ cm^2)	σ_e/σ_g	**Fs** (J·cm^{-2})	λ (μm)	technique	condensed phase/ solution	ref
[(OC$_{10}$H$_{21}$)$_2$C$_6$H$_3$C≡C]$_4$PorZn	148	12	3.4		0.532	Z-scan (ps)		253
21a			3.3[a]		0.532	nonlinear transmission (ns)	CH$_2$Cl$_2$ solution	256
			40[b]					
21b			48[b]		0.532	nonlinear transmission (ns)	CH$_2$Cl$_2$ solution	256
21c			46[b]		0.532	nonlinear transmission (ns)	CH$_2$Cl$_2$ solution	256
21d			34		0.532	nonlinear transmission (ns)	CH$_2$Cl$_2$ solution	256
21e			27[a]		0.532	nonlinear transmission (ns)	CH$_2$Cl$_2$ solution	256
			45[b]					
(CH$_3$C$_6$H$_4$)$_4$PorPCl$_2$			3.56[c]	0.618	0.532	DFWM and Z-scan	CHCl$_3$ solution	261
			12.15[d]					
Os$_3$(μ-H)$_2$(CO)$_9$(μ_3-NIn(III))TPP		38	2.86		0.532	Z-scan (ns)	CH$_2$Cl$_2$ solution	268
TPPIn(III)N$_3$		44	4.57		0.532	Z-scan (ns)	CH$_2$Cl$_2$ solution	268
(phenyl)$_4$TBPorZn[e]		72[f]	4.2		0.532	nonlinear transmission (ps)	benzene solution	270
(phenyl)$_4$TBPorNi[e]		16[f]	1.06		0.532	nonlinear transmission (ps)	benzene solution	270
(phenyl)$_4$TBPorPt[e]		34[f]	2		0.532	nonlinear transmission (ps)	benzene solution	270
(thienyl)$_4$TBPorZn[e]		90[f]	-		0.532	Z-scan (ns)	CH$_2$Cl$_2$ solution	271
		150[g]	15					
(phenyl)$_4$TBPorZn[e]		90[f]	1		0.532	Z-scan (ns)	CH$_2$Cl$_2$ solution	271
		130[g]	14.4					
14a (polymer)		2500[g]	1.4		0.532	nonlinear transmission (ps)	PMMA thin film	272
14a (monomer)		160[g]	4.8		0.532	nonlinear transmission (ps)	PMMA thin film	272
26 (M = H$_2$)	209					Z-scan (ns)	toluene solution	279
26 (M = Ni)						Z-scan (ns)	toluene solution	279
26 (M = Zn)	92					Z-scan (ns)	toluene solution	279
26 (M = Cu)	200					Z-scan (ns)	toluene solution	279
26 (M = Co)						Z-scan (ns)	toluene solution	279

[a] Cross section ratio for the singlet state. [b] Cross section ratio for the triplet state. [c] Estimated from picosecond data. [d] Estimated from nanosecond data. [e] TBP, tetrabenzoporphyrin. [f] Cross section for the singlet state. [g] Cross section for the triplet state.



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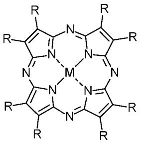
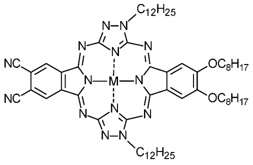
tution at the porphyrazine ring.



25 R = C_6H_5Br
R = $C_6H_5NO_2$

Other different phthalocyanine analogues that have been investigated for their nonlinear behavior are the metallotriazolehemiporphyrazines **26**.[279] Z-scan experiments were performed on solutions of these hemiporphyrazines in order to ascertain the effect of the central metal and the substituents on their nonlinear absorption and refraction properties. An effective tuning of the nonlinear absorption and refraction can be achieved in triazolehemiporphyrazines by introducing different metals into the cavity. However, functionalization of the ring does not seem to affect the nonlinear response.



26

Subphthalocyanines have also shown nonlinear absorption properties. Trineopentyloxy-subphthalocyanine spin-coating films have been measured via the Z-scan technique. Reverse saturable absorption at 532 nm and two-photon absorption at 1.064 μm were observed.[280]

The main performance parameters are listed in Table 6. Only a few of them are reported in each experiment, and comparison is difficult. Values of σ_e/σ_g up to 48 (higher than those for Pcs) have been reached (ns pulses) at 0.532 μm. Different ratios are obtained for a compound when nanosecond or picosecond pulses are used. This suggests the need for a better theoretical analysis.

6. Concluding Remarks

Major advances have been made during the last 10 years in the design and synthesis of phthalocyanines and related materials for NLO. They provide useful examples to illustrate the new features of the NLO response of 2D (and even 3D) systems in comparison with the more thoroughly investigated 1D compounds. This review summarizes the results recently obtained on the correlation between molecular structure and NLO response and offers some strategies for rendering new systems with improved NLO properties.

At this point it is necessary to remark that the comparison between NLO processes (mostly third order), wavelength regimes, measurement techniques, and investigators is tenuous. This is a basic problem in all nonlinear studies. Any reader of a review on this topic needs to come away with these cautionary thoughts dominant in mind to cast the correct perspective on the information the authors are presenting.

As for second-order applications, EFISH and HRS experiments on a variety of phthalocyanines and analogues have provided some useful design criteria for achieving a large response in those 2D systems. First of all, the presence of conjugated linkers between the donor and/or acceptor groups and the macrocyclic core enhances the second-order response in both Pcs and porphyrins. High polarizability values have already been obtained that are comparable to those found for efficient 1D systems. It has also been ascertained that the response depends on the specific peripheral site for the donor/acceptor substitution. However, for reaching the perfomance of the best linear compounds, additional efforts have to be developed for the optimization of 2D molecules. Moreover, the ratio between diagonal and off-diagonal components of the β tensor can be modified through the symmetry of the peripheral substitution pattern. In this way the dipolar/octupolar character of the response can be controlled as theoretically predicted. Axial substitution provides an alternative means to cause asymmetry in Pcs and, so, induce a second-order response. The few results available in solution and films show significant although moderate performances. There are hardly meaningful data about the role of metal complexation on the second-order hyperpolarizability. Some data indicate an increase in β for metal atoms with higher polarizability.

As for the methods to obtain ordered macroscopic molecular assemblies, LB films offer the best perspectives. In particular, the results obtained with Langmuir and LB films of chiral Pc derivatives **7** stand out. They provide interesting clues on the role of supramolecular organization.

For strongly push–pull Pc systems, a three-level (and even a two-level) model associated with the lowest energy (Q band) transitions accounts for the main trends of the SHG response. However, more refined models should be used to account for many relevant features, such as the role of metal substitution.

On the other hand, SubPcs have been shown to present very interesting features for NLO. Although they show a permanent dipole moment associated with the B-halogen axis, the optical response is essentially associated with charge transfer inside the macrocycle plane. Due to the D_{3h} symmetry of this core, the NLO behavior becomes mostly octupolar. In accordance with previous results on octupolar systems, the hyperpolarizabilities of SubPcs reach large values that are even superior to those found for TATB, RuTB, and RuTP. An additional advantage is that due to the permanent dipole moment they can be easily ordered through electrical (e.g. corona) poling. Synthetically speaking, these molecules are still in their infancy, so that the application of the design criteria that have been successful in phthalocyanines and porphyrins may lead to superior second-harmonic generators.

For third-harmonic generation (and other third-order processes) in phthalocyanines and analogues, it is difficult to give a complete rationalization of the factors governing the response. Moreover, the theoretical analysis is more complicated than that for SHG, and a four-level model, including a parity-forbidden two-photon transition, has been found necessary to account for the wavelength dispersion of THG in some metallophthalocyanine films. On the other hand, a number of data indicate that complexation of Pcs and porphyrins with open-shell transition metals enhances the THG (and DFWM) yield. In particular, the model by di Bella predicting larger hyperpolarizabilities for open-shell than for closed-shell complexes has been invoked to account for some data in tetraphenylporphyrins. However, to fully understand this effect and rule out dispersion effects, one should perform detailed wavelength-dependent experiments including off-resonant conditions. On the other hand, axial substituents on the central metal (e.g. Ti) seem to be quite effective in enhancing the third-order response.

Among the nonlinear optical applications of phthalocyanines, optical limiting has emerged as a particularly promising one. The electronic structure is adequate for such an objective, and a five-level model appears adequate to account for the main trends. The most evident conclusion obtained from the various reports on the OL behavior of phthalocyanines and analogues is that the insertion of heavy atoms into the ring causes a significant increase of the reverse saturable absorption. In addition, the introduction of bulky axial substituents has a positive effect in suppressing the aggregation of the macrocycles, giving rise to a more effective nonlinear absorption of the material. Extension of the π-conjugation also seems to enhance the OL response. However, the data are very fragmentary, and more systematic experiments should be performed to better understand the physical mechanisms.

In conclusion, one could say that structural variations explored in phthalocyanines, such as metal insertion, introduction of functional groups into the periphery of the macrocycle, extension of conjugation, and variation of the main structure of the macrocycle, allow the tuning of the nonlinear responses. However, a detailed understanding of the factors affecting the nonlinear response is still necessary, and further work should be devoted to this objective.

7. Acknowledgments

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