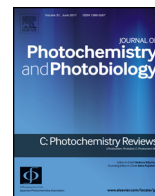




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Conjugated macrocyclic materials with photoactivated optical absorption for the control of energy transmission delivered by pulsed radiations

Mário J.F. Calvete^{a,*}, Danilo Dini^{b,*}^a CQC, Department of Chemistry, Faculty of Science and Technology, University of Coimbra, Rua Larga, P 3004-535 Coimbra, Portugal^b Department of Chemistry, University of Rome "La Sapienza", P.le Aldo Moro 5, I-00185, Rome, Italy

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ABSTRACT

The control of the transmission of the energy transported by optical waves is of extreme importance for the realization of those advanced technologies which require high speed of operation and fast switching. Such a task can be approached through the design and preparation of materials that possess modulable optical properties. In the present review the aspect of material science behind the realization of the effect of optical limiting, OL (or optical power limiting, OPL), will be considered focusing on those materials based on conjugated metallo-macrocycles like porphyrins, phthalocyanines and derivatives. The choice of these molecular materials for OL purposes is motivated by the fact that the optical properties of such annulated systems can be finely modulated in a controlled fashion by changing the chemical structure of the complex. These changes involve the variation of the central metal, the extent of electronic conjugation of the ring, the nature and the number of peripheral ligands, and the eventual introduction of axial ligands coordinated by a central metals with a valence higher than +2. An attempt will be made to establish relationships between the structure of the macrocyclic complex and the relative OL properties taking into account the most recent developments in the field. During this analysis we will also discuss the aspect of optically passivity, i.e. the characteristic of the OL materials of undergoing fast changes of optical properties according to an internal mechanism of self-activation.

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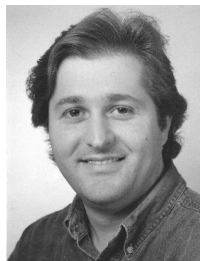
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* Corresponding authors.

E-mail addresses: mcalvete@qui.uc.pt (M.J.F. Calvete), danilo.dini@uniroma1.it (D. Dini).



Mario J. F. Calvete received his Industrial Chemistry diploma from University of Coimbra in 2000 and his Ph.D. in Natural Sciences—Organic Chemistry in 2004, from Eberhard Karls University of Tübingen, Germany, supervised by Prof. Michael Hanack, with a thesis on the field of the synthesis of phthalocyanine derivatives for NLO (Optical Limiting). After a two-year stay at Tübingen as a postdoctoral fellow, working in related fields of Optical Limiting, he returned to Portugal for a postdoctoral stay at University of Aveiro, working on the synthesis of porphyrin–phthalocyanine dyads. In 2010 he was appointed as Auxiliary Researcher at University of Coimbra. He is also Invited Auxiliary Professor, and his current research interests are in tetrapyrrolic macrocycle design and other heterocyclic ligands and their uses in homogeneous/heterogeneous catalysis, theranostics, and light-driven applications. He has published ca. 70 peer-reviewed papers in international journals, 2 books, and 8 book chapters.



Danilo Dini obtained his Ph.D. in Materials Science in 1998 at the University of Rome LA SAPIENZA presenting a thesis on the electrochemical synthesis and chemical-physical characterization of conducting polymers with electrochromic properties. His Ph.D. mentor was Professor Franco Decker. In the postdoctoral time Dini dealt initially with the analysis of the electrochemiluminescent properties of conjugated systems in liquid dispersions and in the immobilized state at Fritz-Haber-Institut of the Max Planck Gesellschaft in Berlin-Dahlemdorf. Successively, the almost serendipitous encounter with Professor Michael Hanack in 2001 led Dini to consider the beautifully blue-colored phthalocyanines as a class of conjugated materials for an application quite more diverse than electrochemistry: nonlinear optics. In the successive five years spent in Tuebingen at the Institut für Organische Chemie of its university, Dini developed some synthetic skills and, more importantly, became progressively more confident with pulsed lasers for the characterization of conjugated macrocycles in the particular sector of optical limiting. In this context, Dini collaborated with several research groups from Europe, the U.S., and Singapore. Before joining the University of Rome in 2010 as research group leader, Dini got involved in the study of semiconductors with nanostructured features for a variety of electronic applications including not only nonlinear optics but also solar energy conversion. For the realization of this last part of research, Dini was hosted by Professor Johannes Gerhard Vos at the School of Chemical Sciences of Dublin City University in Ireland's capital. Dini has authored and coauthored more than 110 papers.

1. Introduction

The nonlinear optical (NLO) effect of OL consists in the attenuation of the intensity of the light transmitted by a system when the intensity of the light exceeds a system-specific threshold value (I_{lim}) [1]. For a given system the response of the transmitted light intensity (I_{out}) vs. the incident light intensity (I_{in}) varies with the wavelength λ of the incident light. Therefore, the optical system will be limited in the range of wavelengths within which it can exert an OL action.

Since the system undergoes a transition from the regime at constant transmittance (we recall here the definition of transmittance, $T = dI_{out}/dI_{in}$) when $I_{in} < I_{lim}$, to the regime with $T \rightarrow 0$ when $I_{in} \geq I_{lim}$, it is implicit that the mechanism of light absorption of the system will necessarily vary in the diverse regimes of optical transmission [2–18]. In particular, the OL effect produced by the molecular materials here considered, i.e. phthalocyanines (Pcs) [19,20], porphyrins (Pors) [21–23] and their analogues [24–27], is based on the mechanism of excited state absorption (ESA), which involves the populating of an excited electronic state possessing an absorption cross-section (σ_{exc}), expressed in cm^2 , larger than the one of the ground electronic state (σ_g) at the wavelength of irradiation [28]. Such an effect has been also denominated reverse saturable absorption (RSA) [29] and is commonly described in terms of the four-level model for molecular systems with NLO activity [30]. The latter model considers the succession of two electronic transitions starting from different electronic states of the molecule, the occurrence of which requires the intervention of a fast process of intersystem crossing with respect to the duration of the radiation. The OL active molecule absorbs one photon initially from its ground

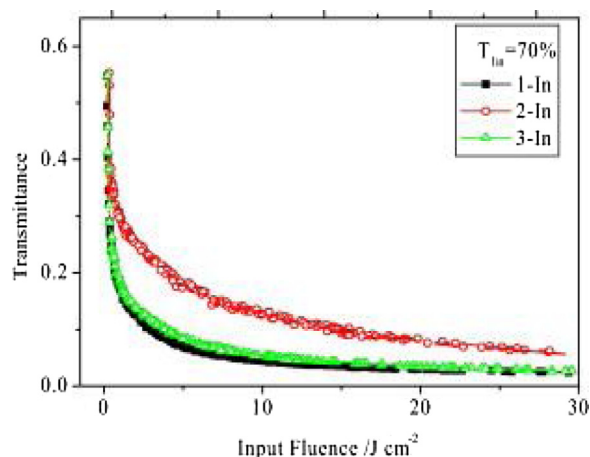


Fig. 1. Typical decreasing trend of the optical transmission of three different OL active materials with the incident fluence (F_{in}). The comparison shows in a straightforward way the stronger OL effect exerted by the compounds associated to the black and green profiles. The indexes 1-In, 2-In and 3-In in the inset refer to the dendrimeric phthalocyanines 17–19 (Chart 3, *vide infra*). Reproduced from ref. [40] with permission of Elsevier.

electronic state to the first excited singlet state. Successively the excited molecule absorbs a second photon at the same energy of the first one either from the singlet excited state or from the first excited triplet state that is populated via an intersystem crossing (ISC) process. The multiphoton absorption here considered in the four-level model takes place in a sequential fashion but events of simultaneous two- or three-photon absorption [31] from ground or excited levels can also occur [26,32]. The four-level model takes into account the characteristic of the NLO active molecule of possessing electronic states with discrete energy levels [33], but the scheme can be applied with success also for the rationalization of the OPL effect produced by semiconducting crystals with electronic band structures [34]. In the four-level model the effective absorption cross-section σ_{eff} in the NLO regime of OL activity at a given wavelength is expressed by the formula [35]:

$$\sigma_{eff} = (\sigma_g I_{lim} + \sigma_{exc} I_{in}) / (I_{in} + I_{lim}) \quad (1)$$

with

$$I_{lim} = h\nu / \sigma_g \tau_{exc} \quad (2)$$

In Eq. (2) h is the Planck's constant, ν the optical frequency, and τ_{exc} the lifetime of the light-absorbing excited state. For the evaluation of the OL effect generated through ESA several figures of merit have been defined [36]. These are directly proportional to the excited state absorption cross-section like in case of the parameters $(\sigma_{exc} - \sigma_g)$ or σ_{exc} / σ_g [30,37]. Other figures of merit for OL performance evaluation can be also defined if the temporal response of the OL system needs to be considered as well [38]. The OL effect is directly evaluated through the main NLO experimental technique of the measurement of the optical transmittance of the OL active material with a light-probe of monochromatic character having modulable intensity/fluence [39]. The OL effect can be visualized through the profile of the optical transmission at a given wavelength of analysis (y -axis) vs. the intensity or fluence of the incident light (I_{in} or F_{in} on the x -axis, Fig. 1) [40].

2. Phthalocyanines and related compounds for optical limiting: some recent examples

Pcs and related compounds are molecular dyes with high molar extinction coefficient in the NIR-visible range. This class of complexes is commonly employed as colorant for traditional and

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