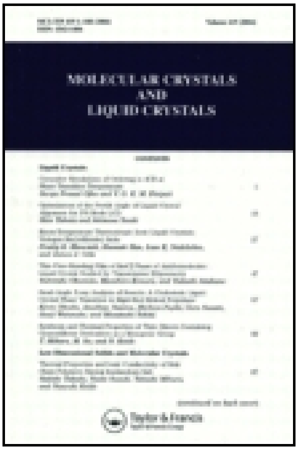

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Optical Limiting of Transition Metal-Phthalocyanine Complexes: A Photochromic Effect involving the Excited State of the Conjugated Molecule

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Optical Limiting of Transition Metal-Phthalocyanine Complexes: A Photochromic Effect involving the Excited State of the Conjugated Molecule

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The nonlinear optical effect of optical limiting which is produced upon high intensity irradiation in the visible spectrum of an optical system containing phthalocyanines is a photochromic event. The photoswitching process at the basis of the optical limiting effect in phthalocyanines is the increase of the optical absorption of the conjugated complex at the wavelength of irradiation following the formation of a highly absorbing excited electronic state of phthalocyanines. The intensity of the optical fields that provoke optical limiting effect in phthalocyanines can be as high as several megawatts per square centimeter. In the present contribution the optical limiting effect generated by phthalocyanines against nanosecond laser pulses in the visible range is reported and analyzed in terms of the structural features of the photoactive molecule. Phthalocyanines with varied structural elements, e.g., different ring-substituents, coordinating central atoms and axial ligands, could be prepared through various synthetic strategies. The analysis of the optical limiting properties of the various phthalocyanines has been carried out under conditions which could allow a meaningful comparison of their actual effectiveness.

Keywords: optical limiting; photochromism; photoswitching; phthalocyanine; pulsed laser; reverse saturable absorption

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INTRODUCTION

The development of advanced technologies designated to exploit and/or control the energy of the luminous radiation into a desirable way has to be based on the possibility offered by special materials of varying opportunely their optical properties in a controlled fashion. The switching of the absorptive and refractive properties of a material in the UV-vis-NIR can be achieved through all the mechanisms which lead to the alteration of the electronic states of the material with energies ranging in the broad interval 1–4 eV. Of particular relevance are the switching phenomena involved in photochromic [1], electrochromic [1a,2] or nonlinear optical (NLO) processes (Fig. 1) [3], because in these processes the switching factor is the electromagnetic field, i.e., a parameter which can be controlled to a great extent and modulated within a wide range of intensities and frequencies [4].

The switching mechanisms induced by the application of intense electric fields for NLO effects have stimulated great interest for the role that nonlinear optics plays in the emerging field of photonics [5]. In fact, photonics involves the use of short-pulsed laser [6] for the light-speed storage and processing of informations carried through photons [7], which requires the utilization of typically NLO effects like

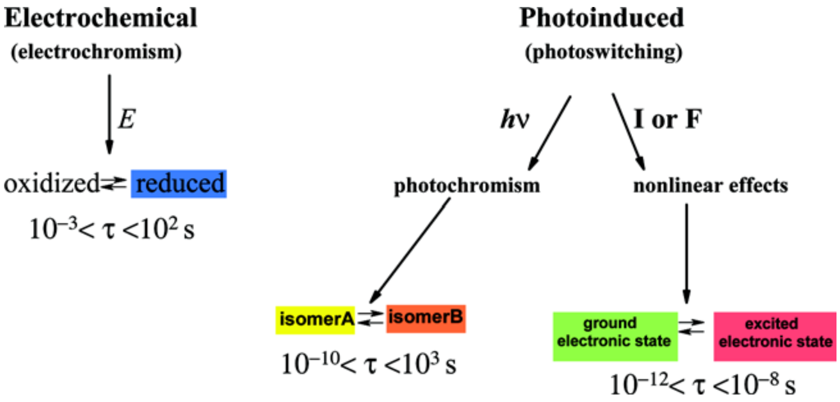

FIGURE 1 Switching mechanisms of the optical properties of materials through static and rapidly variable electromagnetic fields. E represents the static electric field for the electrochromic switching, hν is the energy associated with the electromagnetic radiation producing the photochromic switching, I and F are respectively the intensity and fluence of the electromagnetic radiation producing the NLO switching, and τ is the generic time constant for the different switching mechanisms operating on light absorbing materials.

optical switching or light-frequency conversion. Such NLO phenomena [3a,3b] are induced in switching materials upon their interaction with high-intensity radiations like those produced by short-pulsed lasers.* Under these circumstances the irradiated materials can modify their absorptive, refractive and emissive properties within the limits of its photochemical stability [8].

Among NLO phenomena, reverse saturable absorption (RSA) [9] producing optical limiting (OL) [10] of intense short-pulsed laser radiations constitutes an important effect which can be exploited for the protection of light-sensitive elements operating below a safety threshold of intensity [9b,11]. The RSA properties of several classes of materials have been studied and characterized [9a,9b,12]. In particular, chromophores like the metal complexes of phthalocyanines (Pc's) and analogues (Fig. 2) have proved to be especially effective optical limiters through RSA mechanism [13] (Fig. 3) for their fast response and high optical absorption in NLO regime due to the presence of an extended network of conjugated π-electrons [14]. In fact, a network of conjugated electrons in delocalized π-type orbitals infers high electronic polarizability, fast charge redistribution when the Pc complex interacts with rapidly variable intense electromagnetic fields, and, additionally, gives rise to several electronic transitions from ground and from excited states, which are responsible for the occurrence of OL (Fig. 3).

In the following the NLO properties of a series of titanyl [15], vanadyl [16] and ruthenium [17] phthalocyaninato complexes dissolved in liquid solution will be described and compared. The analysis of the results is carried out taking into account the structural features which accompany the largest variations of optical transmission in the NLO regime imposed by nanosecond laser pulses at 532 nm.

RESULTS

The variations of the optical transmission for the series of complexes tetrapyrazinotetraazaporphyrinato titanium oxide ($Pyr_4TAPTiO$) (**1**), hexadecafluorophthalocyaninato titanium oxide ($F_{16}PcTiO$) (**2**), hexadecachlorophthalocyaninato titanium oxide ($Cl_{16}PcTiO$) (**3**), and hexadecachlorophthalocyaninato titanium dichloride ($Cl_{16}PcTiCl_2$) (**4**), (Fig. 4) are presented in Figure 5. In the experiment of NLO transmission determination of Figure 5 the linear transmission T_0 at 532 nm was $T_0 = 0.80$ for the saturated solutions of (**1**)–(**4**) in

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*The intensity I of a radiation is inversely proportional to the duration Δt of the energy flux since, by definition, is $I = (\Delta E/\Delta t) \times (A)^{-1}$ where ΔE is the energy transferred by the radiation during the time Δt across the irradiated area A.

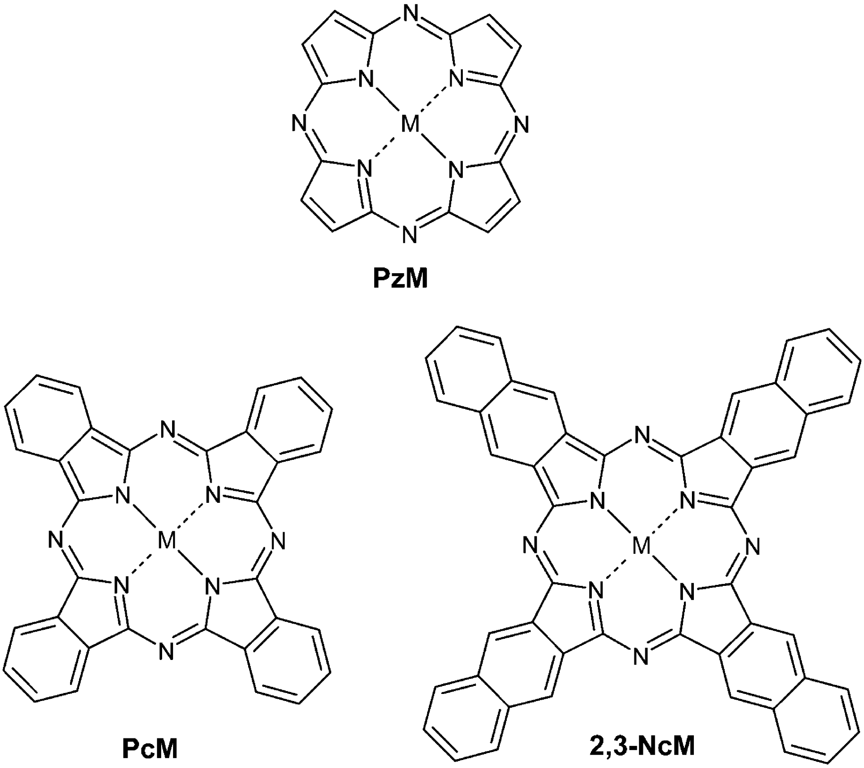


FIGURE 2 Metalloporphyrazine (PzM); Metallophthalocyanine (PcM) and 2,3-Metallonaphthalocyanine (NcM).

chloronaphthalene. Among titanium complexes (**1**)–(**4**) the most effective OL of ns laser pulses has been achieved for the fluorinated complex (**2**) [18], which displays a minimum transmittance of 0.3 at the fluence value 7 J cm^{-2}. Perchlorinated complexes (**3**) and (**4**) have similar OL behavior with $Cl_{16}PcTiCl_2$ (**4**) possessing a wider range of stability with respect to the titanyl counterpart (8 vs. 6 J cm^{-2}). The heteroaromatic complex $Pyr_4TAPTiO$ (**1**) shows a variation of NLO transmission which strongly resembles those of the perchlorinated systems (**3**) and (**4**), but with a slightly weaker OL effect.

NLO transmission variations for the vanadyl complexes phthalocyaninato vanadium oxide (PcVO) (**5**), tetrapyrazinotetraazaporhyrinato vanadium oxide (Pyr_4TAPVO) (**6**), hexadecafluorophthalo cyaninato vanadium oxide ($F_{16}PcVO$) (**7**) and hexadecachlorophthalocyaninato vanadium oxide ($Cl_{16}PcVO$) (**8**), (Fig. 6) are shown in

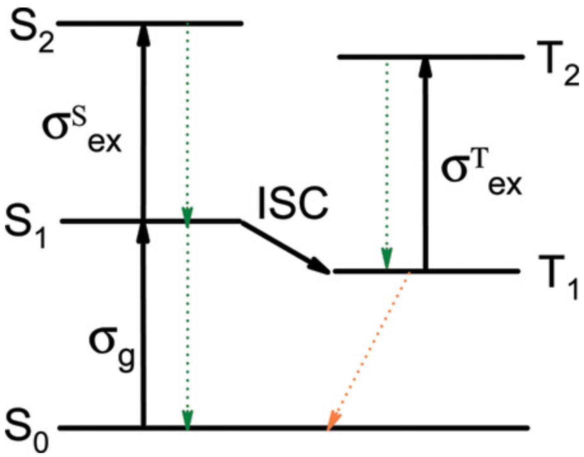


FIGURE 3 Jablonski diagram for the description of the mechanism of reverse saturable absorption (RSA) upon short-pulse irradiation of chromophores like phthalocyanines, in the visible spectrum. S_0, $S_{1(2)}$ and $T_{1(2)}$ indicate the ground singlet state, the first (second) excited singlet state and the first (second) excited triplet state, respectively. The chromophore absorbs the first photon through the transition $[S_0 \rightarrow S_1]$, and, depending on the dynamics of the irradiated system, will absorb sequentially a second photon through either $[S_1 \rightarrow S_2]$ or $[T_1 \rightarrow T_2]$ transition. $\sigma_{ex}^{S(T)}$ and σ_g are the absorption cross-sections from the excited singlet (triplet) state and the ground state, respectively. Verification of RSA implies that $\sigma_{ex}^{S(T)} > \sigma_g$. Orange and green arrows indicates phosphorescence and fluorescence decays, respectively. ISC is the acronym for intersystem crossing $[S_1 \rightarrow T_1]$. For sake of clarity only the fundamental vibrational level of the various electronic levels is indicated.

Figure 7. The NLO transmission curves of the vanadyl complexes (**5**)–(**8**) (Fig. 7) have been determined for the saturated solutions in chloronaphthalene being T_0 (532 nm) = 0.80 for all four solutions of (**5**)–(**8**). Similar to the trends observed within the series of titanium complexes (**1**)–(**4**) (Fig. 5), the most effective OL of ns laser pulses has been achieved with the perfluorinated complex (**7**) (Fig. 7) [18]. Pyr_4TAPVO (**6**) and the perchlorinated vanadyl complex (**8**) displayed similar OL behavior with $Cl_{16}PcVO$ (**8**) showing a larger range of photostability with respect to (**6**) (8 vs 7 $J\,cm^{-2}$). The OL effect produced by unsubstituted PcVO (**5**) is intermediate between the perfluorinated complex (**7**) and Pyr_4TAPVO (**6**). Chloronaphthalene as a dissolving medium displays some NLO absorption as shown by the decrease of transmission upon irradiation of the sole solvent (Figs. 5 and 7) [19].

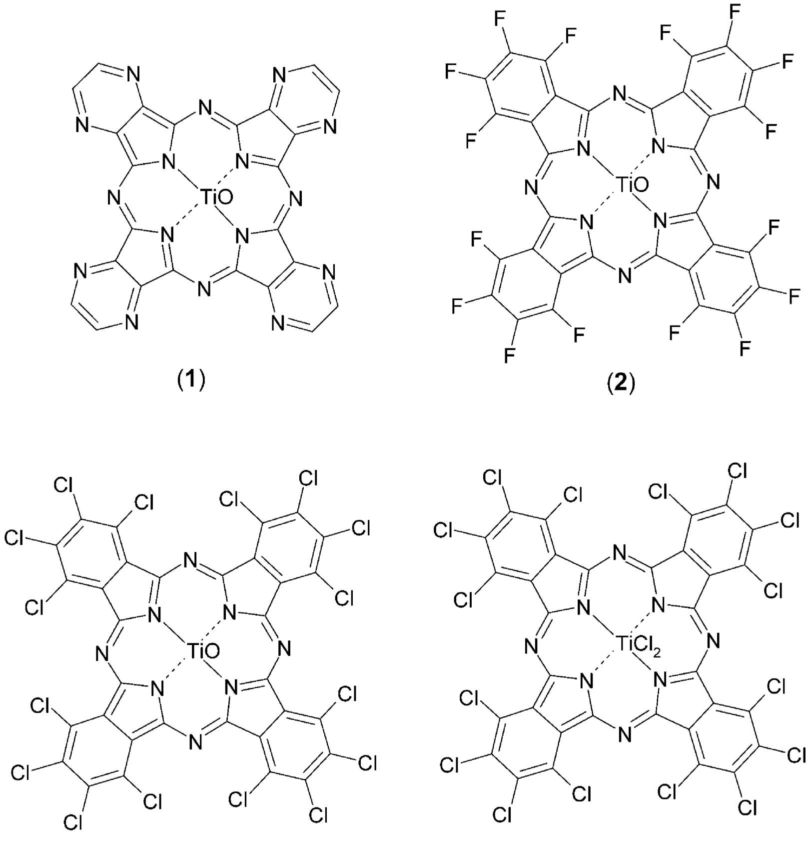

(1) (2) (3) (4)

FIGURE 4 Titanium phthalocyanine complexes $Pyr_4TAPTiO$ **(1)**, $F_{16}PcTiO$ **(2)**, $Cl_{16}PcTiO$ **(3)** and $Cl_{16}PcTiCl_2$ **(4)** for NLO transmission studies.

Another group of phthalocyanine complexes whose NLO transmission has been determined is the series of complexes: ruthenium phthalocyanine (PcRu) (**9**), 2,(3)-tetratertbutylphthalocyaninato ruthenium (*t*-Bu_4PcRu) (**10**) and hexadecafluorophthalocyaninato ruthenium ($F_{16}PcRu$) (**11**) (Fig. 8). The NLO transmission curves of ruthenium complexes (**9**)–(**11**) (Fig. 9) have been determined in their pyridine solution (concentration range: $7–10^{*}10^{-5}$ M), being T_0 (532 nm) = 0.88 for all three solutions of (**9**)–(**11**). Different to the axially substituted complexes (**1**)–(**8**), the series of ruthenium complexes (**9**)–(**11**) has shown quite scarce dependence on the nature of the peripheral substituent (Fig. 9). Similar to the trends observed at 532 nm

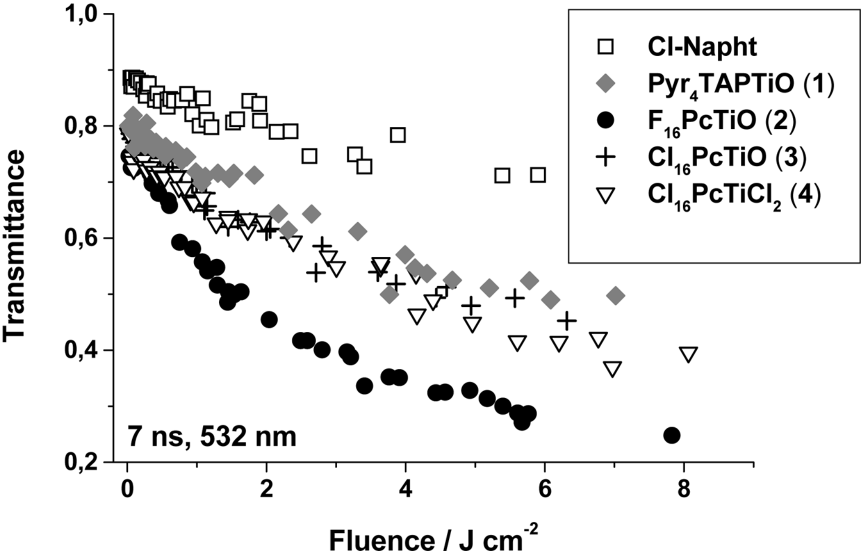
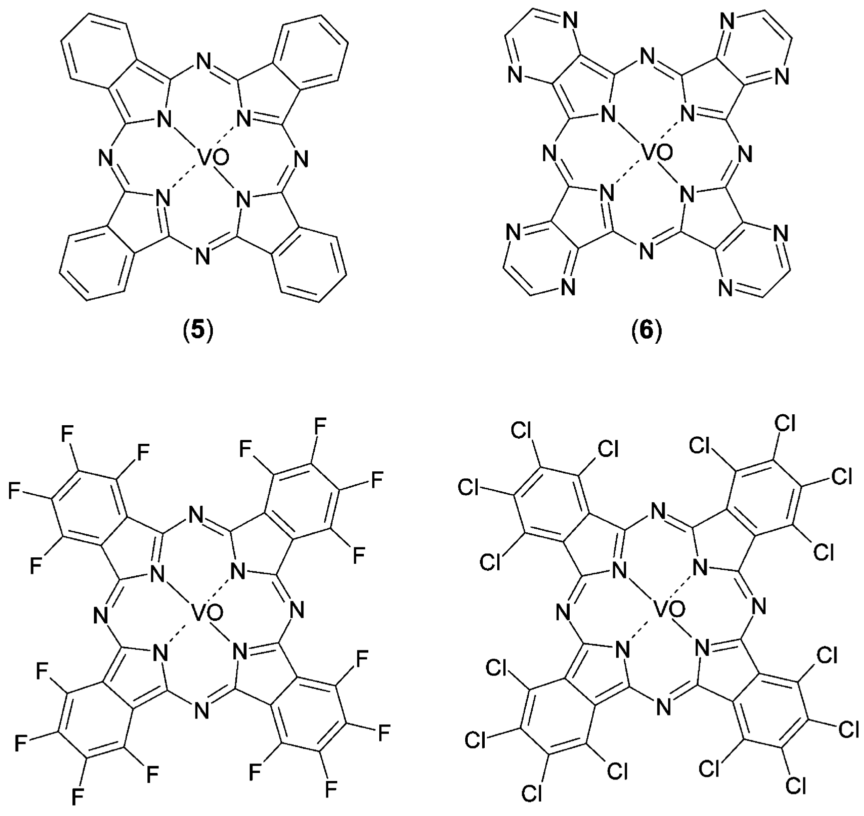


FIGURE 5 Variation of the optical transmission versus the incident fluence at 532 nm for various axially substituted titanium phthalocyanines (**1**)–(**4**) with different peripheral substituents. The duration of the laser pulses was 7 ns. Measurements were carried out in saturated solutions of (**1**)–(**4**) in chloronaphthalene.

(Fig. 9) are the variations of NLO transmission of (**9**)–(**11**) at 1064 nm (Fig. 10). Beside the generally small decrease of optical transmission for all three species (**9**)–(**11**) upon intense irradiation at 1064 nm, it is also evident a poor dependence of the NLO transmission variation on the nature of the peripheral substituent in the three ruthenium complexes (**9**)–(**11**). T_0 (1064 nm) was 0.90 for (**9**)–(**11**) solutions in pyridine. The experiments at 532 and 1064 nm were run on the same solutions of (**9**)–(**11**) in pyridine.

DISCUSSION

The series of phthalocyanine complexes (**1**)–(**11**) have proved to behave as reverse saturable absorbers at 532 nm in liquid solution when the incident fluence F_{in} ranges in the interval 1–10 J cm^{-2} for nanosecond laser pulses. This is because the optical transmission at 532 nm always decreases with the increase of F_{in} although to a different extent for the various complexes (Figs. 5, 7 and 9). In the same interval of F_{in} a weak effect of reverse saturable absorption could be verified also at 1064 nm in the case of ruthenium complexes (**9**)–(**11**) (Fig. 10) [20]. For all



(5) **(6)**

(7) **(8)**

FIGURE 6 Vanadyl phthalocyanine complexes PcVO **(5)** Pyr_4TAPVO **(6)** $F_{16}PcVO$ **(7)** and $Cl_{16}PcVO$ **(8)** for NLO transmission studies.

complexes (**1**)–(**11**) the occurrence of such nonlinear optical phenomenon at 532 nm is due to a mechanism of sequential two-photon absorption (Fig. 3). In this case an excited electronic state is formed upon absorption of the first photon, and it absorbs at the same wavelength more efficiently than the ground state [14b–f]. In the case of phthalocyanines (**1**)–(**11**) it has been observed that such an excited state absorbs light pulses with duration of several ns (pulse duration range: 3–10 ns). This implies that the lifetime of the absorbing excited state cannot be shorter than 10 ns for the whole series of phthalocyanines (**1**)–(**11**) in the adopted experimental conditions. If the absorbing excited state is not directly formed upon absorption of the first photon from the ground state, then the internal conversion time τ_{IC}, i.e., the

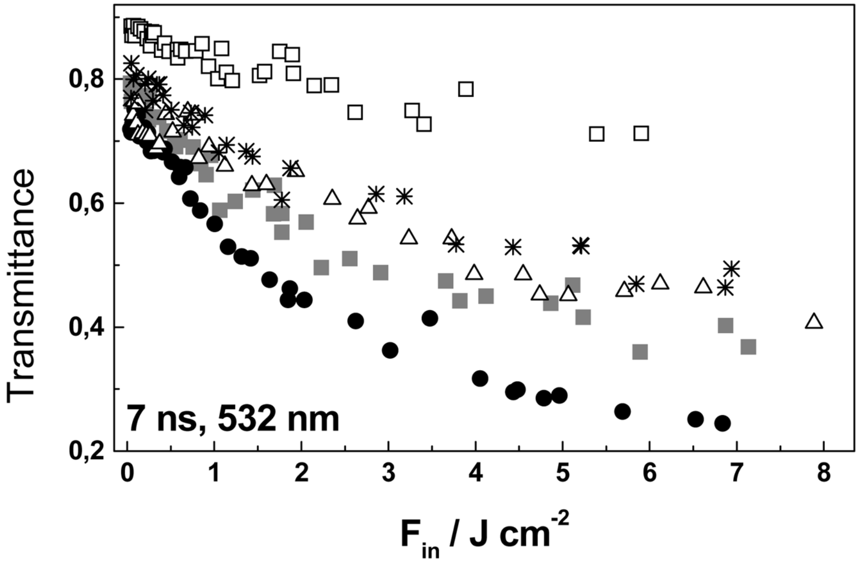
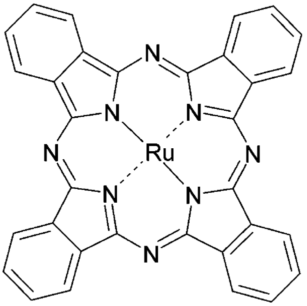


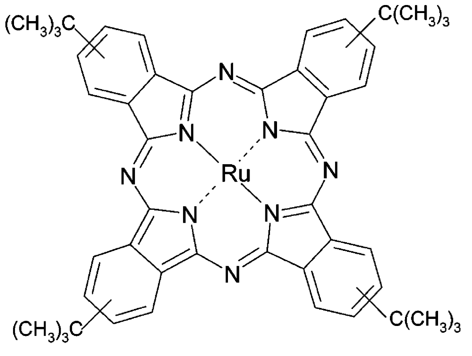
FIGURE 7 Variation of the optical transmission versus the incident fluence at 532 nm for vanadyl phthalocyanines (**5**)–(**8**) with different peripheral substituents. Chloronaphthalene (□), PcVO (**5**) (■), Pyr$_4$TAPVO (**6**) (∗), F$_{16}$PcVO (**7**) (•) and Cl$_{16}$PcVO (**8**) (△). Duration of laser pulses was 7 ns. Measurements were carried out in saturated solutions of (**5**)–(**8**) in chloronaphthalene.

time necessary for the system to be transformed into the absorbing excited state, has to be shorter than the pulse duration, i.e. $\tau_{IC} < 3$–10 ns. In phthalocyanines internal conversion is probably an intersystem crossing process in which the formation of the absorbing excited state determines a change of spin state after absorption of the first photon (Fig. 3) [8b].

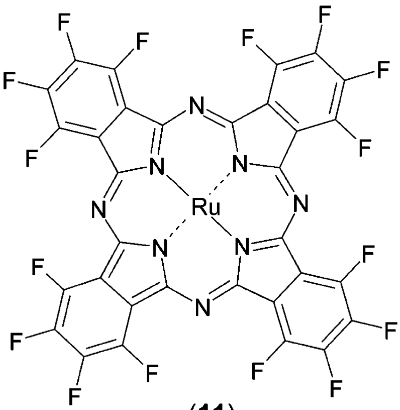
The comparison of the NLO transmission curves for the series of titanyl and dichlorotitanium phthalocyanine complexes (**1**)–(**4**) (Fig. 5) reveals that the pattern of peripheral substitution for **1** and **3** (Fig. 4), and the nature of the axial ligand for **4** does not affect considerably the OL performance of these complexes in saturated solutions with the exception of F$_{16}$PcTiO (**2**). A possible reason for that could be the presence of a larger concentration of **2** with respect to **1, 3** and **4** in saturated chloronaphthalene solution, which leads to a larger number of excited state absorbers per unit volume of solution and, consequently, a larger number of absorbed photons under the same flux of luminous power (OL differences due to concentration effect). As a matter of fact, the perfluorinated titanyl complex **2** has



(9)



(10)



(11)

FIGURE 8 Ruthenium phthalocyanine complexes PcRu **(9)**, *t*-Bu_4PcRu **(10)** and F_{16}PcRu **(11)**, for NLO transmission studies.

the larger solubility among the series of titanium phthalocyanines **1–4**. Such a feature can imply also a lower extent of molecular aggregation in solution [14g] with consequent favourable effect on the duration of the excited state lifetime [14b]. In addition to that, it has been also verified that the presence of electron-withdrawing substituents like fluorine , which are characterized by a relatively high *charge-to-atomic volume* ratio, can enhance the OL properties of the phthalocyaninato complex through larger variations of the transition dipole moment which is associated with the absorption of the excited state of axially substituted phthalocyanines [14f,18,20b]. In conclusion, **2** has to be considered the best optical limiter within the series (**1**)–(**4**),

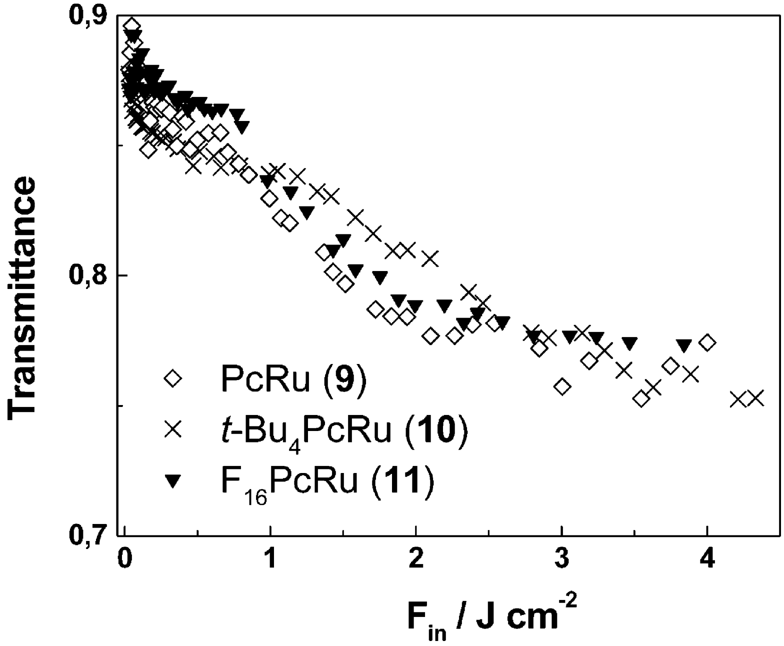


FIGURE 9 Variation of the optical transmission versus the incident fluence at 532 nm for ruthenium phthalocyanines (**9**)–(**11**). Duration of laser pulses was 7 ns. Measurements were carried out in pyridine as solvent. The range of concentration values for (**9**)–(**11**) in pyridine was 7–9*10^{-5} M.

since the linear transmittance for the saturated solutions of (**1**)–(**4**) was the same ($T_0 = 0.80$) with **2** displaying the larger optical attenuation (Fig. 5).

Analogous considerations can be drawn in the analysis of the NLO behavior at 532 nm of the series of vanadyl complexes (**5**)–(**8**), in which the perfluorinated system **7** displays the stronger OL effect (Fig. 7).

Phthalocyaninato ruthenium complexes (**9**)–(**11**) do not show substantial differences in the OL behavior at both 532 and 1064 nm despite of the remarkable differences in the electronic nature of the peripheral substituents. Such finding points out that the variations of the transition dipole moments from the ground as well as the excited state of (**9**)–(**11**) are not influenced by the electronic properties of the peripheral substituent. A possible explanation for that could be the absence of any considerable deformation of the electronic clouds during the occurrence of the various transitions at the basis of OL effect in such complexes. This is justified by the relatively high electronic polarizability of the central metal ruthenium which is more

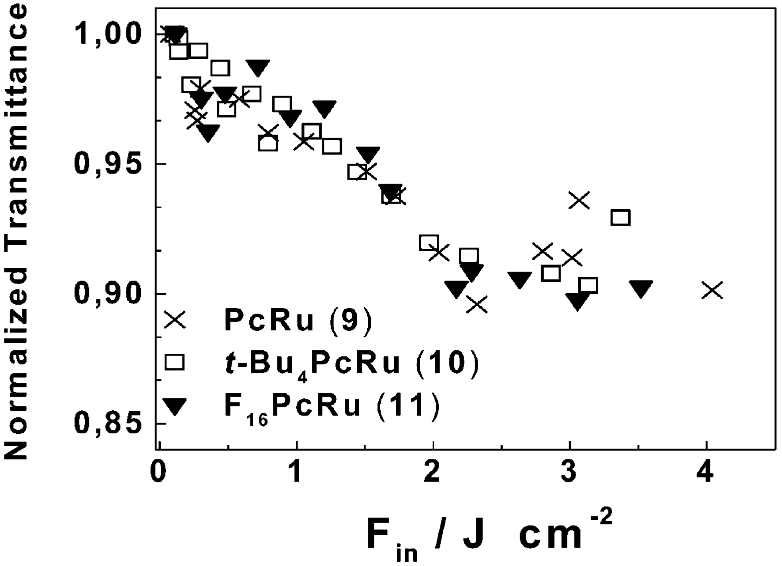


FIGURE 10 Variation of the optical transmission versus the incident fluence at 1064 nm for ruthenium phthalocyanines (**9**)–(**11**). Duration of laser pulses was 7 ns. Measurements were carried out in pyridine as solvent. The range of concentration values for (**9**)–(**11**) in pyridine was like in the experiments of Figure 9.

electron-rich than vanadyl and titanyl central moieties [16]. As far as OL of **9–11** at 1064 nm is concerned, it is believed that the mechanism at the basis of reverse saturable absorption is simultaneous two-photon absorption [20b] rather than excited state absorption [20a]. This is because it is quite improbable that an electronic excited state generated in NLO regime, i.e. at high incident optical power, absorbs also at lower energies values with respect to the same system in the ground state which is, by definition, the most stable electronic state. In fact, in the linear spectra of **9–11** no further absorption appears at wavelengths longer than 690 nm (or energies lower than 1.8 eV), like 1064 nm. The threshold of absorption at 690 nm in the ground state of **9–11** is associated with the transition of the Q-band in these phthalocyanines. The photogenerated excited states of **9–11**, i.e., states with relatively less stability, cannot absorb effectively at wavelengths higher (or energies lower) than the ones corresponding to Q-band absorption (around 690 nm) of the ground state since excited electronic states have generally a wider HOMO-LUMO gap with respect to the ground state [14b]. These considerations rule out the possibility that the excited state which is responsible for OL of **9–11** at 532 nm is the same which is eventually responsible for the weak OL of **9–11** at 1064 nm.

EXPERIMENTAL

Synthesis

The synthesis of the two pyrazino derivatives $Pyr_4TAPTiO$ (**1**) and Pyr_4TAPVO (**6**) has been accomplished according to the following procedures. $Pyr_4TAPTiO$ (**1**) is prepared by heating a mixture of 2,3-pyrazinedicarbonitrile (1.3 g, 1×10^{-2} moles) and titanium(IV)butoxide (1 g, 3×10^{-3} moles) at 130°C for six hours. The reaction mixture is washed with hot methanol, filtered and successively dried under vacuum at 80°C overnight. The resulting bluish-greenish powder is then heated at 220°C under vacuum for 16 hours. Pyz_4TAPVO (**6**) [21] is prepared by refluxing a solution of 2,3-pyrazinedicarbonitrile (1.3 g, 1×10^{-2} moles) and vanadium(III)chloride (0.6 g, 3.8×10^{-3} moles) in pentanol (2 mL) at 120°C for 4 hours. The solution is filtered and the filtrate is washed with hot methanol. The filtrate is dried under vacuum at 80°C overnight to remove the solvent. The resulting bluish-greenish powder is then heated at 220°C under vacuum for 30 hours. Perfluorinated $F_{16}PcTiO$ (**2**) and $F_{16}PcVO$ (**7**) were prepared and characterized according to the experimental procedures described in Ref. [18].

Perchlorinated $Cl_{16}PcTiO$ (**3**) has been prepared through an adaptation of the procedures described in Ref. [22] and [23]. The perchlorinated dichloroderivative $Cl_{16}PcTiCl_2$ (**4**) has been synthesized according to the procedure presented in Ref. [24] by replacing phthalodinitrile (in the original work) with tetrachlorophthalodinitrile as starting material.

Similar to the procedure reported for the preparation of Pyz_4TAPVO (**6**), the vanadyl phthalocyanines PcVO (**5**) and $Cl_{16}PcVO$ (**8**) have been prepared in analogous conditions using as starting materials phthalodintirile [25] and tetrachlorophthalodinitrile, respectively.

Ruthenium complexes PcRu (**9**), *t*-Bu_4PcRu (**10**) and $F_{16}PcRu$ (**11**) were prepared according to the synthetic procedures reported respectively in Ref. [26], [27] and [28].

NLO Measurements

The light source used for the determination of NLO transmission of phthalocyanines (**1**)-(**11**) was a pulsed Nd:YAG laser whose second and first harmonics of emission have been used. The incident beam had a gaussian profile and the pulse duration was in the range 5–10 ns. In all the experiments of NLO transmission determination the optics of incidence of the gaussian beam was f/65 [29]. The choice of such "slow" optics was done purposely in order to minimize heating effects during the Z-scans in the open aperture configuration [30], which were run for the determination of the experimental points of the curves in Figures 5, 7, 9 and 10 [14b]. The NLO properties of the liquid solutions of the species (**1**)–(**11**) were analyzed in quartz optical cell with thickness 1 mm. In the evaluation of NLO transmission at 532 nm (Figs. 5, 7, and 9) the waist of the laser beam was 40 μm in correspondence of the focus, whereas the beam waist was 60 μm at the focus of the gaussian beam for the experiment at 1064 nm (Fig. 10). The time stability of the liquid samples for NLO experiments has been checked through the following three procedures: daily check of the linear optical spectrum of the sample; comparison of the OL measurements obtained when pulse repetition rate was 10 Hz and when the sample was irradiated with a single shot; irradiation of the sample solution with laser pulses at a fixed energy with a repetition rate of 10 Hz for thirty minutes and successive check of the OL properties. Solvent effects on the OL of the sample solution were studied by measuring OL of the pure solvent. Solvents for NLO experiments were used without further purification (commercial spectroscopic grade). Calibration of the optical apparatus was conducted using reference samples of C_{60} and carbon nanotubes as standards. The OL properties of the different samples are characterized in the same conditions of irradiation and compared with those of the standards.

CONCLUSIONS

It has been found that titanyl, dichlorotitanium, vanadyl and ruthenium phthalocyanines **1–11** carrying different kind of peripheral substituents display reverse saturable absorption at 532 nm in the nonlinear optical regime imposed by nanosecond pulses. Such an effect is ascribed to a mechanism of excited state absorption in which an excited state (presumably a triplet state) absorbs at 532 nm more efficiently than the ground state of the same system. It is found that the lifetimes of the excited states of phthalocyanines **1–11**, which absorb at 532 nm in nonlinear optical regime is longer than 10 ns, i.e., the maximum duration of the laser pulse. Compounds **1–11** require less than few ns to form the excited state whose absorption gives rise to the observed optical limiting effect. It is thus demonstrated that optical limiting at 532 nm is a photochromic effect which involves the transformation of the system from a low-absorbing ground state to a highly–absorbing excited state when **1–11** are irradiated with ns pulses. Reverse saturable absorption displayed by ruthenium complexes **9–11** at 1064 nm for ns pulses is attributed to simultaneous two-photon absorption rather than to excited state absorption after considering the spectral features of **9–11** in the linear and nonlinear optical regimes.

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