Demonstration of the optical limiting effect for an hemiporphyrazine†

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The hemiporphyrazine complex 9,22-bis(dibutoxy)hemiporphyrazinato chloroindium(III) (1) is one of the few examples for this class of compounds, which displays the nonlinear optical effect of reverse saturable absorption for nanosecond laser pulses in the visible spectrum. The high linear transmission combined with the fast switching into a strongly absorbing excited state in the same spectral range (400–650 nm), renders the studied hemiporphyrazine an ideal material for the passive shuttering of pulsed radiations.

The quest for materials displaying optical power attenuation properties in the visible spectrum is mostly motivated by interest in the practical realization of optical limiting (OL)[1] devices (optical limiters) which protect light-sensitive sensors, *e.g.* eye or CCD cameras, from possible damage caused by intense light exposure. The function of an OL device operating in a predefined spectral range is to warrant high transmission of the radiation within this range when the radiation intensity is lower than the safety threshold of the optical sensor, and to block the transmission of the incident radiation once its intensity exceeds such a safety threshold. In particular, if an optical limiter is designed for the protection of the eye,[2] the photoactive material producing the OL effect must be highly transparent and strongly absorbing in the visible spectrum when the incident energy density is below and above 1 μJ cm^{-2}, respectively.[3] Among the several classes of materials displaying OL effect in the visible spectrum[4] phthalocyanines (Pcs) and naphthalocyanines (Ncs)[5] are particularly attractive for their ability to respond *reversibly* and *passively* in the ns or ps range,[6] their potential *broadband* action against frequency-agile lasers[7] and their photochemical *resistance* against radiation induced fatigue.[8] For eye-protecting limiters,[9,10] high transparency in the linear optical regime is generally desired and Pcs can afford that through the expansion of the Pc ring into a Nc[11] since such a transformation produces complexes with a wider range of high linear transmission in the UV/Vis by shifting the strong Q-band of Pcs towards NIR.[12]

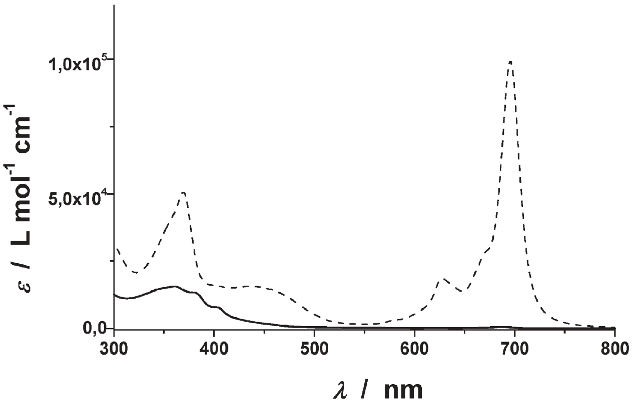
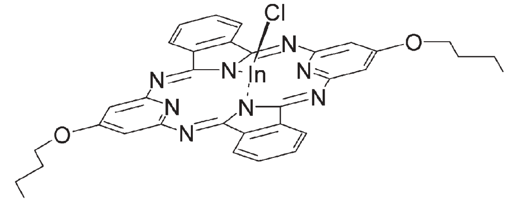


Fig. 1 Molar extinction coefficients (ε) of 9,22-bis(dibutoxy)hemiporphyrazinato chloroindium(III) (**1**) (full line) and 2,3-octa-(2-ethyl-hexyloxy)-phthalocyaninato chloroindium(III) for comparison (dashed line) in the UV-visible. Solvent: toluene.

As an alternative strategy to Pc ring expansion in order to enlarge the high transmission window in the visible we use here for the first time an hemiporphyrazine (Hp), *i.e.* a system with a lower extent of conjugation with respect to Pcs. Hps can be synthesized through the condensation of two 1,3-diiminoisoindolines with two 2,6-diaminopyridine molecules.[13] Similar to Pcs, Hps are tetra-azadentate ligands which can coordinate a large variety of central atoms or divalent groups, but possess a reduced symmetry (C_{2v}) of the unsubstituted ligand with respect to the Pc ring (D_{4h}). The main effects of such structural features in Hps are the predominant absorption in the near UV (Fig. 1),[14,15] and fluorescent emission in the visible region[16] whereas Pcs emit in the NIR.[14c,14d,17] The combination of such linear optical features with the possible verification of reverse saturable absorption (RSA)[18] in the visible by Hps based systems would lead to the fulfilment of some of the most decisive conditions for the actual development of eye-protecting limiters.[1,2] In the present study [9,22-bis(dibutoxy)hemiporphyrazinato] chloroindium(III) [$\mathrm{(BuO)_2HpInCl}$, **1**, Scheme 1] was taken[13h] since the presence of two alkoxy groups as peripheral substituent on the pyridine rings would impart solubility and processability to complex **1** (substituents on isoindoline moieties would produce the same effect of solubilization).[13i] In addition, the



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Scheme 1 9,22-Bis(dibutoxy)hemiporphyrazinato chloroindium(III) (**1**)[13h] for nonlinear optical transmission studies.

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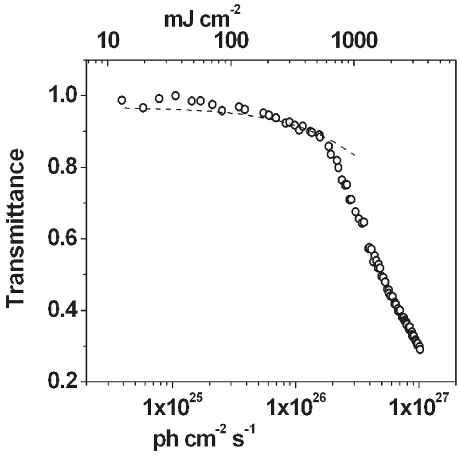

Fig. 2 Nonlinear transmittance of 1×10^{-4} M toluene solution of $(BuO)_2HpInCl$ (**1**) at 532 nm using 9 ns pulses. Linear transmittance of **1** at 532 nm: 0.99. The dashed line shows a fitting obtained with a model which accounts for a one photon absorbed from the ground state and one from an excited triplet state with absorption cross section σ_T=16 × 10^{-17} cm^{-2}.

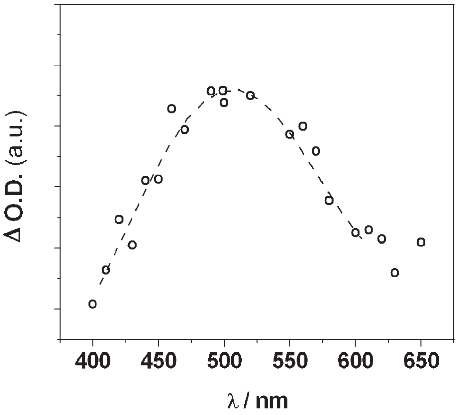

Fig. 3 Differential absorption spectrum of 1.0 × 10^{-4} M $(BuO)_2HpInCl$ (**1**) in toluene determined with pump and probe experiments. For each wavelength, points have been extracted from the temporal profiles of absorption of **1** at 100 ns after the laser pulse. Excitation of **1** was produced with laser pulses at 532 nm with 9 ns duration and incident intensity 1.13 × 10^{26} photons cm^{-2} s^{-1}. Dashed line is an aid to the eye.

presence of indium as central atom in $(BuO)_2HpInCl$ (**1**) is expected to induce favourable effects[5b,5c] on the mechanism of sequential multiphoton absorption in which efficiently pumped excited triplet states absorb photons more effectively than the ground state at the wavelength of irradiation[19] in the nonlinear optical regime.

The solution of $(BuO)_2HpInCl$ (**1**) with linear transmittance T_0 = 0.99 at 532 nm (ε = 218 L mol^{-1} cm^{-1} and σ_0 = 0.83 × 10^{-18} cm^2, being ε and σ_0 the ground state molar extinction coefficient and absorption cross-section, respectively) displays nonlinear optical behaviour at this wavelength starting at about 2.0 × 10^{25} photons cm^{-2} s^{-1} as the value of incoming photon flux (Fig. 2). In correspondence of such a value the transmittance of $(BuO)_2HpInCl$ (**1**) solution diminishes in a reversible fashion and shows a rapid decrease when incident intensity values get larger than 2.0 × 10^{26} photons cm^{-2} s^{-1} thus giving rise to the effect of RSA.‡ Compound **1** displays an OL action against ns long pulses at 532 nm with the transmission of 29% of the total incident fluence (F_{in}) when it reaches the maximum value F_{in} = 3.5 J cm^{-2}. This corresponds to F_{out} = 1.05 J cm^{-2} (F_{out} is the output fluence) at the minimum transmittance (T_{min}) displayed by **1**. The limiting threshold, which is defined as the fluence transmitted by the sample when T/T_0 = 0.5 (T and T_0 are the nonlinear and linear transmittance, respectively), is 1.5 J cm^{-2}. $(BuO)_2HpInCl$ (**1**) does not show any considerable variation of the linear UV-Vis spectrum after nonlinear transmission measurement, thus indicating that sample degradation does not take place after occurrence of this nonlinear optical effect. For the determination of the excited state spectrum of $(BuO)_2HpInCl$ (**1**) (Fig. 3) pump and probe experiments were conducted on a 1 × 10^{-4} M solution of **1** in toluene pumping with the same nanosecond laser pulses at 532 nm used for recording the nonlinear transmission. In order to bring $(BuO)_2HpInCl$ (**1**) into a nonlinear optical regime the intensity of the pump radiation was set at 1.13 × 10^{26} photons cm^{-2} s^{-1}, corresponding to the intensity value at which the onset of larger nonlinear optical behavior of **1** is verified (Fig. 2). Nanosecond long pulses at 532 nm pump complex **1** into a highly absorbing excited state in the range 400–650 nm with a maximum of absorption at about 500 nm similar to what is found for Pcs in a triplet excited state (Fig. 3).[5c] Moreover, we have found that the excited absorbing state shows a lifetime of about 500 ns, in the presence of oxygen which usually shortens it. This indicates that $(BuO)_2HpInCl$ (**1**) is one of the few examples of Hps which possesses long living excited states and displays reverse saturable absorption.[20] These findings lead to the conclusion that also in the case of $(BuO)_2HpInCl$ (**1**) an intersystem crossing process operates for the generation of a triplet excited state of **1** which absorbs more effectively than in the ground state within the spectral range 400–650 nm. One should also observe that the nonlinear behaviour of $(BuO)_2HpInCl$ (**1**) is similar to that of Pcs, but the abrupt decrease of the nonlinear transmittance above 2.0 × 10^{26} photons cm^{-2} s^{-1} shows that an absorption process with more than one photon is active at higher intensities in the triplet manifold, since a smoother variation is expected when only one photon is absorbed by the triplet states. In fact, we have found that only the first part of the non linear transmission curve, up to 2.0 × 10^{26} photons cm^{-2} s^{-1}, can be fitted with a model which accounts for one-photon absorbed from the ground state and a second one from a triplet state (see Fig. 2). The verification of these characteristics for $(BuO)_2HpInCl$ (**1**) discloses the use of this new class of complexes as photoactive materials with high potential for passive optical switching through nonlinear optical phenomena.[1,2,4] This is mainly a consequence of the high linear transmission of $(BuO)_2HpInCl$ (**1**) in the visible range and the high nonlinear absorptivity in the same spectral range when **1** is irradiated with nanosecond laser pulses. Further modification of the structure for this type of molecules is expected to bring useful results for the realization of OL devices for the protection of eyes.[20]

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Notes and references

‡ The small band centered at about 680 nm in Fig. 1 indicates the presence of unsubstituted PcInCl that is formed during the ring condensation conditions of $(BuO)_2HpInCl$ (**1**). PcInCl could not be completely removed from **1** upon column chromatography. The presence of PcInCl is further verified when the fluorescence spectrum of **1** is analyzed. In fact, beside the strong emission at about 450 nm from **1** another emission appears at about 700 nm from PcInCl. From these data the percentage of PcInCl as an impurity in **1** appears to be very low ($< 0.1\%$). We have verified that the observed variations of nonlinear transmittance (Fig. 2) do not depend on the presence of such an impurity since controlled addition of unsubstituted PcInCl in a solution of **1** did not alter the nonlinear optical behavior of these more concentrated solutions in PcInCl with respect to the solution solely of **1**.

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