

Nonlinear Optical Properties of Tetrapyrazinoporphyrazinato Indium Chloride Complexes Due to Excited-State Absorption Processes

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The multiphoton absorption properties of the axially substituted tetrapyrazinotetraazaporphyrinato complex Pyz₄TAPInCl (**1**) are reported and interpreted. In particular, the nonlinear optical transmission of the complex and the excited states involved in the nonlinear absorption have been determined at the frequency of the second harmonic generation of a Nd:YAG laser in the nanosecond time regime. Pyz₄TAPInCl has an excited-state absorption cross section larger than its ground state in the 460–540 nm spectral region, and it shows an optical limiting (OL) behavior at 532 nm, which derives from a sequential two-photon absorption with a larger absorption cross section of the excited triplet state with respect to the ground state. It results that the absorption cross section of **1** in the excited triplet state is $7.8 \times 10^{-18} \text{ cm}^2$ vs $0.9 \times 10^{-18} \text{ cm}^2$ of the ground state at the wavelength of OL analysis.

Introduction

The heteroaromatic tetrapyrazinotetraazaporphyrin (Pyz₄TAP) is a conjugated macrocycle characterized by the presence of eight nitrogen atoms occupying the 1, 4, 8, 11, 15, 18, 22, and 25 positions of the ring (Figure 1).^{1,2} Linstead and co-workers prepared complexes of this type already in 1937,¹ but, up to now, besides metal-free Pyz₄TAPH₂ only a few other examples of metallated tetrapyrazinotetraazaporphyrins have been reported.^{1–4} Besides their employment as charge-transfer materials in xerographic processes⁵ and as discotic mesophases for liquid crystal displays,⁶ Pyz₄TAP-type compounds have been also studied for nonlinear optical (NLO) applications,^{4,7} namely, optical limiting (OL).⁴

In comparison to phthalocyanines (Pcs), the external eight nitrogen atoms of Pyz₄TAPs (Figure 1) induce strong electronic effects on the complex structure.⁴ In particular, one finds that the central cores of Pyz₄TAPs are less electron-rich than the corresponding phthalocyanines,^{2f} and a blue shift of the main optical absorption bands in their UV–vis spectra is observed.⁴ A relatively larger shift of the Q-band ($a_{1u} \rightarrow e_g$ transition) and a smaller shift of the B band ($a_{2u} \rightarrow e_g$ transition) toward higher energies (or smaller wavelengths) were also obtained by Hückel/molecular orbital (MO) calculations of Pyz₄TAP^{2–} for which the a_{1u} orbital is mostly localized on the external nitrogen atoms, whereas e_g and, to a much less extent, a_{2u} orbitals only partially extend over these atoms.^{2f,4} The comparison between the geometries and the energy levels of the frontier molecular orbitals of an axially substituted Pc and Pyz₄TAP are presented in Figure 2.⁴

The evolution of the excited-state absorption features in passing from a Pc to an analogous Pyz₄TAP complex has not been yet reported. In fact, the excited-state spectra of porphyrins,⁸ Pcs,^{9–11} and naphthalocyanines (Ncs),¹² which are pro-

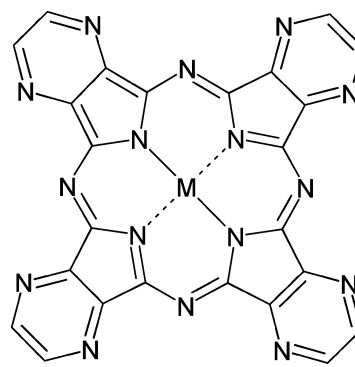


Figure 1. Metallo tetrapyrazinotetraazaporphyrin (Pyz₄TAPM).

duced upon absorption of short laser pulses in the UV–vis region, show a broad absorption with a maximum located approximately at the center of the spectral interval comprised between the B- and Q-bands of the linear spectrum. However, it is not yet known whether the presence of heteroatoms on Pyz₄TAPs still produces a similar excited-state spectrum or not. For such a reason, we have synthesized the axially substituted Pyz₄TAPInCl (**1**) and evaluated its OL properties, since the presence of an axial substituent is a desirable structural feature for the realization of efficient OL materials¹³ and indium as a central metal is known to be particularly effective in these complexes for the same purpose.^{9,10} Pump and probe experiments were performed to characterize the excited states involved in the multiphoton absorption processes related to the OL behavior of **1**. The excited-state absorption spectrum of Pyz₄TAPInCl has been determined upon excitation of **1** with nanosecond laser pulses.

Experimental Section

Pyz₄TAPInCl Synthesis. Pyz₄TAPInCl is prepared by heating a mixture of 2,3-pyrazinedicarbonitrile (1.3 g, 1×10^{-2} mol) and indium trichloride (0.65 g, 3×10^{-3} mol) in pentanol (2 mL) at 130 °C for 5 h. The reaction mixture is washed with

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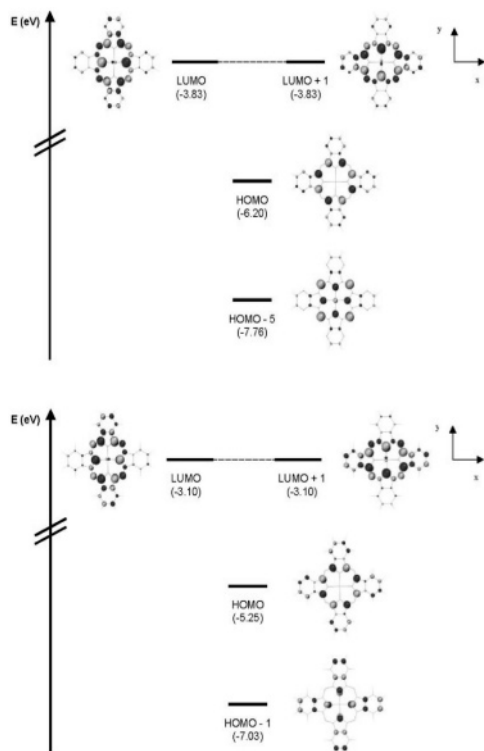
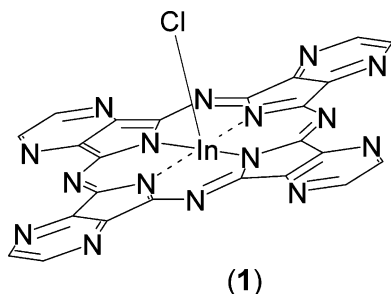


Figure 2. Energies and shapes of the molecular orbitals of an axially substituted Pyz₄TAP (top) and its analogous Pc counterpart (bottom). The size and color of the circles describe the amplitude and the sign of the linear combination of atomic orbital coefficients associated with the π -atomic orbitals (adapted from ref 4).

CHART 1: Tetrapyrazinotetraazaporphyrinato Indium Chloride Pyz₄TAPInCl (1)



hot methanol, filtered, and successively dried under vacuum at 80 °C overnight. The resulting blue-green powder is further heated at 220 °C under vacuum for 16 h. ¹³C NMR: sharp peak at 150.2 ppm (1×10^3 Hz). CP/MAS ¹H NMR: broad peak centered at 8.2 ppm (1.5×10^3 Hz). MS (MALDI-TOF): 672.9 Da (molecular peak, 670.71 Da). IR (in KBr pellet; cm^{-1}): 3316.89 (very broad), 1741.18 (sharp), 1664.22 (broad), 1625.15 (sharp), 1525.60 (sharp), 1364.10 (sharp), 1213.45 (sharp), 1364.10 (sharp), 1213.45 (sharp), 1194.91 (shoulder), 1100.13 (broad), 1063.58 (shoulder), 907.99 (sharp), 871.03 (broad), 840.38 (sharp), 755.45 (sharp), 738.04 (sharp), 650.78 (sharp). Elemental analysis: found 41% C (theoretical, 42.98% C); found 32% N (theoretical, 33.41% N); found 2.5% H (theoretical, 1.20% H). Discrepancies within the order of a few percent between the experimental results and theoretical values of the composition of Pyz₄TAPs, PCs, and their derivatives as determined with elemental analysis can be found.^{4,14} This is because of the high thermal stability of these classes of compounds^{14a,14b} and the general low volatility of unsubstituted PCs and Pyz₄-

TAPs, which do not allow a complete combustion of these under elemental analysis experimental conditions.

NLO Transmission Measurements. Nonlinear optical transmission measurements were carried out with 9-ns pulses at 532 nm of a doubled Nd:YAG laser (Quantel YG980E). Transmitted energies were measured with a pyroelectric detector (Scientech model SPHD25) at 2 Hz in an open-aperture configuration. Intensity of the incident pulses was controlled with a $\lambda/2$ wave plate and a polarizing cube beam-splitter. The pulse area on the sample was 0.050 cm^2 . The measurements were done with 2-mm-thick glass cells. Solutions of Pyz₄TAPInCl used for the experiments were 7×10^{-3} M in dimethylsulfoxide (DMSO) and showed a linear transmission of $T_0 = 0.48$ at 532 nm ($\epsilon = 228 \text{ L mol}^{-1} \text{ cm}^{-1}$). Linear optical spectra have been recorded with a Varian Cary 5 UV-vis spectrophotometer.

Pump and Probe Experiments. In these experiments, a solution of 2.1×10^{-3} M Pyz₄TAPInCl in DMSO was excited with the same pulses used for the NLO measurements at 150 mJ cm^{-2} . White light generated by a stabilized 250-W tungsten lamp was used as a probe. A 1-GHz digital oscilloscope (LeCroy LC564A) was allowed to record the transient signals observed with a Jobin-Yvon Horiba TRIAX 320 spectrometer, equipped with an Hamamatsu phototube (R2257).

Results

The NLO transmission of a 7×10^{-3} M DMSO solution of Pyz₄TAPInCl, using 9 ns pulses at 532 nm, is reported in Figure 3. Nonlinear behavior is observed at incident fluence (F_{in}) values higher than about 80 mJ cm^{-2} . A minimum transmission of 0.19 was recorded in correspondence with $F_{\text{in}} = 2100 \text{ mJ cm}^{-2}$. The limiting threshold F_{lim} , i.e., the value of F_{in} at which the actual NLO transmission is equal to one-half of the linear transmission T_0 , is 1200 mJ cm^{-2} .

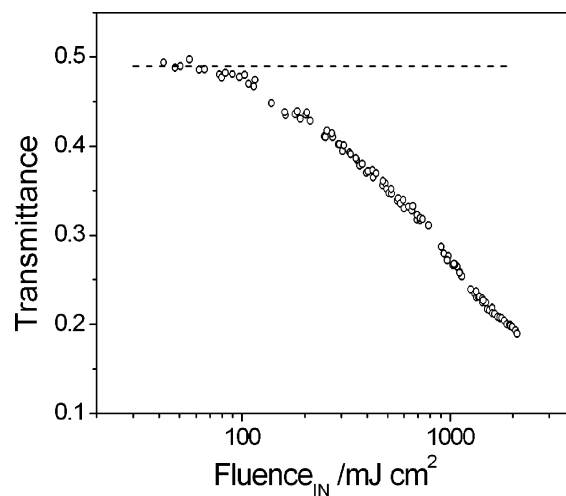


Figure 3. Nonlinear optical transmission of a 7×10^{-3} M DMSO solution of Pyz₄TAPInCl at 532 nm.

To check the photostability of Pyz₄TAPInCl (1), we recorded the linear optical spectrum before and after the measurements of NLO transmission as shown in Figure 4.

We have found that the absorbance at 645 and at 335 nm, i.e., in correspondence with the Q- and B-bands, respectively, were unchanged, whereas the intensities of the vibronic band at 589 nm, of the Q-band shoulder at about 710 nm, and of the featureless region between the Q- and B-bands were generally reduced. These features can be ascribed to a decrease of molecular aggregation of the irradiated solution probably due to the local rising of temperature induced by the laser absorption.

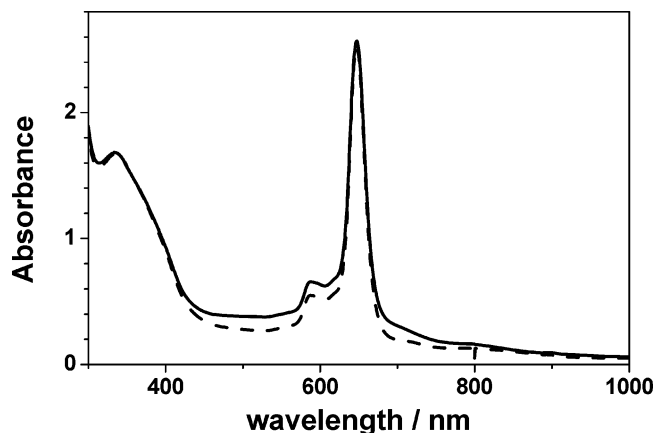


Figure 4. UV-vis spectra of Pyz₄TAPInCl in DMSO before (full line) and after (dashed line) the nonlinear transmission measurements.

An effect like laser-induced convection flow cannot be considered as a cause of the spectral alterations shown in Figure 4. This is because a replenishment of hot solution with cold solution in correspondence with the irradiated area of the sample would have simply led to no spectral change. Moreover, a laser-induced change of the binding energy between the central atom indium and the macrocyclic ligand would have brought about an energy shift of the main absorption bands especially the metal-to-ligand and ligand-to metal charge-transfer bands (not shown in Figure 4), which is not verified. We conclude that Pyz₄TAPInCl (**1**) is a very photostable compound since high-intensity irradiation does not induce any process of decomposition. This finding also demonstrates that **1** possesses higher photostability with respect to analogous Pcs, which would decompose under similar experimental conditions of irradiation.¹⁵ Such differences can be ascribed to the presence of electronegative nitrogen atoms in the external rings of the macrocycle.^{2e,3,4} The general lower photostability of Pcs with respect to analogous Pyz₄TAPs⁴ has been verified especially in those cases where Pcs have electron releasing groups (ERGs), e.g., alkyl, aryl, oxoalkyl, or thioalkyl, as peripheral substituents.^{13a,15,16} Despite the increase in solubility that such substituents impart to the complex, a major drawback associated with their presence is the lowering of the oxidation potential of the resulting complex. As a consequence of that, at a fixed incident light intensity the ERG-substituted complexes would undergo a faster photooxidation process with respect to an analogous Pyz₄TAP system.

Pump and probe experiments were carried out on a DMSO solution of **1** at different wavelengths to determine the absorption properties of its excited states. In Figure 5, a typical temporal variation of the optical absorption of **1** at 500 nm following the excitation at 532 nm is reported.

One observes, after the pulse, a transient absorption that lasts several tens of microseconds. The data in Figure 5 can be fitted with a monoexponential decay using a time constant of 11.6 μ s. The duration of absorption decay is influenced by the presence of oxygen with which the complex in its triplet state interacts. In the adopted experimental conditions, oxygen was not removed from the solution; therefore, the measured value of the decay constant has to be considered a lower limit for such a process. In deoxygenated solutions, the transient absorption of **1** (not shown) shows a slower decay, thus confirming the assignment of the triplet-triplet absorption. The analysis of the transient absorptions in the spectral region 460–540 nm allowed us to obtain a spectrum of the excited molecules of **1** (Figure 6).

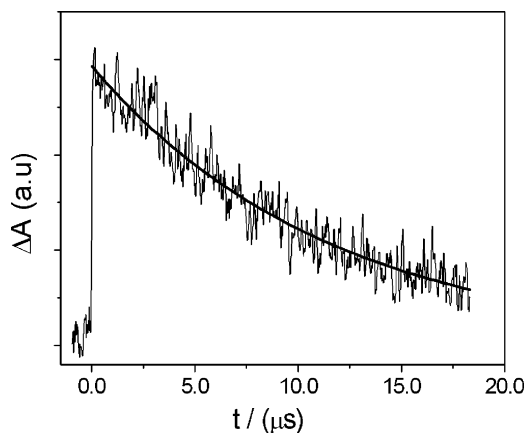


Figure 5. Temporal variation of the optical absorption of **1** in DMSO at 500 nm following the photoexcitation at 532 nm.

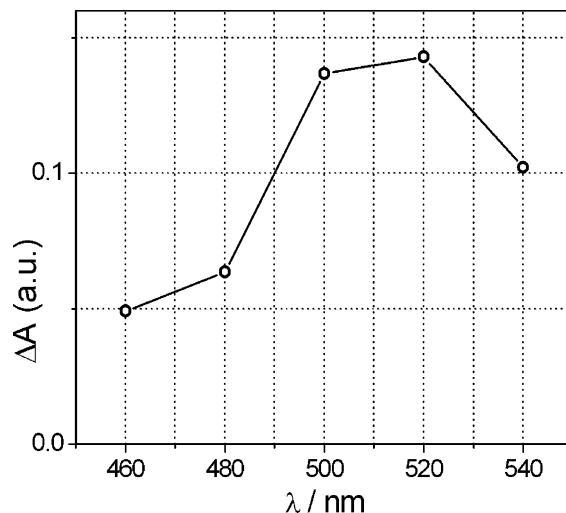


Figure 6. Transient excited spectrum of Pyz₄TAPInCl (**1**) obtained after 300 ns from the exciting pulse.

The excited-state spectrum in Figure 6 is obtained using the signal of the transient absorption at 300 ns after the laser pulse. The excited-state spectrum is typical of the triplet state as commonly found for this type of molecules.⁹ Furthermore, the transient data observed with the maximum achievable resolution in our experiment (about 10 ns) does not allow us to find any other different excited-state spectra also at times shorter than 300 ns. These findings imply two main facts: First, the time necessary to form the triplet highly absorbing state is almost instantaneous on the time scales of nanoseconds.¹⁷ Second, the lifetime of this state is long and can account for the limitation of nanosecond pulses (Figure 5). The evaluation of the triplet formation time will be the object of a future investigation that will involve experiments with shorter laser pulses.

Model for the Nonlinear Optical Absorption

Complex **1** behaves as a nonlinear absorber at 532 nm in DMSO solution when incident fluence F_{in} ranges in the wide interval 80–2000 mJ cm^{-2} (Figure 3). The transient absorption measurements suggest that a mechanism of sequential two-photon absorption like that depicted in Figure 7 can account for this behavior since a large excited-state absorption occurs for microseconds.

In this model, the first photon is absorbed by the transition $S_0 \rightarrow S_1$, and depending on the dynamics of the excited states, a second photon can be absorbed sequentially by either $S_1 \rightarrow$

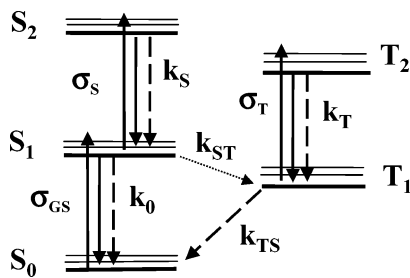


Figure 7. Jablonski diagram for excited-state dynamics of **1** in DMSO. S_0 , $S_{1(2)}$, and $T_{1(2)}$ indicate the ground state, the first (second) excited singlet state, and the first (second) excited triplet state, respectively. σ_i and k_i indicate absorption cross sections and relaxation constants, respectively.

S_2 and/or $T_1 \rightarrow T_2$ transitions. In Figure 7, σ_{GS} , σ_S , and σ_T are the absorption cross sections for the transitions from the ground state, the first singlet state, and the lowest triplet state, respectively, whereas k_0 , k_S , k_T , k_{ST} , and k_{TS} are the relaxation constants to the ground state, to the first singlet state, to the lowest triplet state, for the intersystem crossing, and for the phosphorescence decay from the lowest triplet state to the ground state, respectively.

The set of differential equations describing the dynamics of the ground and excited-state populations are

$$\frac{dN_{S0}}{dt} = -\sigma_{GS}(N_{S0} - N_{S1})I + k_0N_{S1} + k_{TS}N_{T1}$$

$$\frac{dN_{S1}}{dt} = -\sigma_{GS}(N_{S1} - N_{S0})I - k_0N_{S1} - k_{ST}N_{S1} - \sigma_S(N_{S1} - N_{S2}) + k_SN_{S2}$$

$$\frac{dN_{S2}}{dt} = -\sigma_S(N_{S2} - N_{S1})I - k_SN_{S2}$$

$$\frac{dN_{T1}}{dt} = -\sigma_T(N_{T1} - N_{T2})I + k_{ST}N_{S1} + k_TN_{T2} - k_{TS}N_{T1}$$

$$\frac{dN_{T2}}{dt} = -\sigma_T(N_{T2} - N_{T1})I - k_TN_{T2}$$

where N_i are the populations of the states and I is the incident intensity. Solution of this set of equations¹⁸ gives the populations during the laser pulse and, therefore, the absorption deriving from the three types of transitions.

Sequential multiphoton absorption with σ_S , $\sigma_T > \sigma_{GS}$ gives rise to the phenomenon of reverse saturable absorption in which, at higher laser pulse intensities, many molecules are in an excited state and absorb more efficiently than in the linear regime when absorption occurs from the ground state. In phthalocyanines and analogues such as Pyz₄TAPs, it is known that a fast intersystem crossing (ISC) process is usually active,⁹ in which the formation of the absorbing excited state determines also a change of spin state after absorption of the first photon (Figure 7).¹⁹ The observed nonlinear absorption behavior suggests that also in this case the time necessary for the system to be transformed into the triplet state can be shorter than the pulse duration, i.e., $k_{ST}^{-1} < 9$ ns.

For the determination of the various constants described in Figure 7, we have analyzed the experimental data of Figures 3, 4, and 5 concerning the linear and nonlinear optical behavior of **1**. σ_{GS} is measured from the experimental linear absorption spectra at 532 nm, whereas k_0 is known to be less than 1 ns for

indium phthalocyanines.²⁰ k_{TS} is known from the pump and probe experiments, and it is on the order of 10 μ s or larger in the present case. As a matter of fact, its precise value is actually not needed for the nonlinear absorption of 9-ns laser pulses because it is one order of magnitude larger than the pulse and it only shows that there is an accumulation of population in this state during the pulse itself. k_S and k_T (Figure 7) can be considered very fast, of the order of picoseconds, since they are relaxations of higher excited states. The fitting allows one to determine the values of the absorption cross section of the excited singlet state σ_S , of the triplet state σ_T , and k_{ST} , which is the ISC constant determining the overall quantum yield. Figure 8 shows the best fitting that we have obtained using the model of Figure 7.

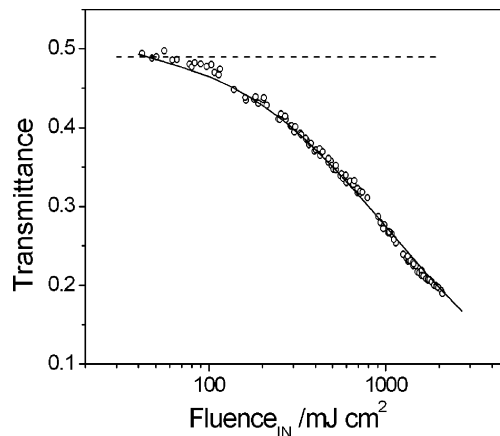


Figure 8. Fitting of the experimental nonlinear transmission data of a 7 mM DMSO solution of Pyz₄TAPInCl (continuous line).

The values of the parameters of the fitting are $\sigma_S = 9.0 \times 10^{-19}$ cm², $\sigma_T = 7.8 \times 10^{-18}$ cm², $k_0 = 3.0 \times 10^9$ s⁻¹, $k_S = 1.0 \times 10^{12}$ s⁻¹, $k_{ST} = 8.0 \times 10^8$ s⁻¹, $k_T = 1.0 \times 10^{12}$ s⁻¹, and $k_{TS} = 8.8 \times 10^4$ s⁻¹ (cf. Figure 7), taking into account that $\sigma_{GS} = 8.0 \times 10^{-19}$ cm². It is found that the most important contribution comes from the triplet manifold where populations accumulate during the laser pulse due to an ISC quantum yield of 21%. A larger contribution from the excited singlet state would have given a different result. This value of the ISC quantum yield is considerably lower than the value found for indium phthalocyanines (more than 75%).⁹ When compared to the value of $\sigma_T(532 \text{ nm}) = 60 \times 10^{-18}$ cm² for the state-of-the-art molecule tetra *tert*-butylphthalocyaninato indium chloride (*t*Bu₄-PcInCl),^{9,10} the corresponding value for Pyz₄TAPInCl is lower. The origin of such a difference can be found in the different electronic structures of the two molecules (Figure 2) and in the different aggregation behavior of the molecules in solution, which affects the dynamics of the excited-state formation and relaxation. Occurrence of molecular aggregation generally decreases the overall efficiency of the OL effect shown by this type of conjugated complexes,²¹ although in some cases the opposite behavior can be also verified.²² It is generally found that Pyz₄TAPs have a stronger tendency of molecular aggregation with respect to analogous Pcs.⁴ This is because Pyz₄TAPs have additional intermolecular dipole–dipole interactions due to a larger presence of polar CN bonds in the molecule.^{21,23} The Pyz₄TAPInCl here considered does not possess any peripheral substituent that would generally make it more soluble in organic solvents or matrixes. As previously discussed, a reason for such a choice is the general verification of decreased photostability in the conditions of NLO transmission determination at 532 nm when alkyl- or aryl-substituted macrocycles are tested.^{13a,15,16}

The OL effect for nanosecond pulses in the UV–vis region (mostly at 532 nm) of a number of phthalocyaninato and naphthalocyaninato indium complexes has been previously determined, namely, for the peripherally substituted systems *t*Bu₄PcInCl, ^{9a,10,13h} F₁₆PcInCl, ^{16a} (C₆H₁₃)₈PcInCl, ^{13h} *t*Bu₄PcIn(*p*-TMP) (*p*-TMP = *para*-trifluoromethylphenyl), ^{9a} *t*Bu₄PcIn(PFP) (PFP = pentafluorophenyl), ^{9a} *t*Bu₄PcIn(acac) (acac = acetylacetonate), ²⁴ (EHO)₈PcIn(acac) (EHO = 2-ethyl-hexyloxy), ²⁴ dimeric axially bridged (*t*Bu₄PcIn)₂O, ^{13h,25} (*t*Bu₄PcIn)O[GaPc(*t*Bu₄)], ^{13h} (*t*Bu₄PcIn)₂(TFP) (TFP = 2,3,5,6-tetrafluorophenylene), ²⁶ (*t*Bu₄PcInCl)₂(dib) (dib = 1,4-diisocyanobenzene), ²⁶ and [*t*Bu₄PcIn(TMP)]₂(dib), ²⁶ trimeric side-by-side [PcIn(acac)]₃, ²⁴ and the naphthalocyanines (BuO)₈NcInCl, ^{12b} *t*Bu₈NcInCl, ^{16a} *t*Bu₄NcInCl, ^{13a} *t*Bu₄NcInI, ^{13a} and (*t*Bu)₄(EHO)₄NcIn(*p*-TMP). ^{13a} Where available for these indium complexes at 532 nm, the ratio σ_T/σ_{GS} (a parameter defined for the comparative evaluation of the OL effect)²⁷ ranges between 10 for dimeric (*t*Bu₄PcIn)O[GaPc(*t*Bu₄)]^{13h} and above 30 for both *t*Bu₄PcInCl¹⁰ and *t*Bu₄PcIn(*p*-TMP),^{9a} whereas Pyz₄TAPInCl (**1**) displays σ_T/σ_{GS} = 8.7 at the same wavelength. This comparison shows that **1** is a worse optical limiter for nanosecond pulses at 532 nm with respect to its peripherally substituted phthalocyanine counterparts. However, it cannot be here concluded that the effects of the replacement of eight carbon atoms with eight nitrogen atoms in the four peripheral rings of a Pc (Figure 1) brings about a worsening of the OL properties in the resulting complex since it should be considered the OL effect of unsubstituted PcInCl²⁸ as an appropriate term of comparison. It has been recently demonstrated by our groups that the structural modification leading to the transformation of an unsubstituted Pc into an unsubstituted Pyz₄TAP actually improves the OL properties at 532 nm for nanosecond pulses as far as axially substituted Pyz₄TAPs such as titanyl and vanadyl tetrapyriznotetraazaporphyrinato complexes were concerned.⁴ It is then expected that a possible comparison between the OL effect for nanosecond pulses at 532 nm of **1** and that of the unsubstituted complex PcInCl would probably lead to a similar result.

Conclusions

It has been found that the tetrapyriznotetraazaporphyrinato indium chloride (Pyz₄TAPInCl, **1**) in DMSO solution behaves as a reverse saturable absorber in the nanosecond time regime at 532 nm similar to phthalocyanines and other Pyz₄TAPs. At a molecular level, the process can be understood in terms of a sequential two-photon absorption mechanism that is characterized by the larger absorption cross section of the triplet–triplet excited-state transition. It is found that the ratio σ_T/σ_{GS} is 8.7 for **1** at 532 nm. Pump and probe measurements have shown that multiphoton absorption can occur in the spectral region around 532 nm where the triplet absorption is larger than that of the ground state. It has also been found that the molecule shows a good photostability against possible light-induced degradation (either oxidation or decomposition), due mostly to the increase of electronegativity associated with the presence of nitrogen atoms in the conjugated ring.

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