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Tetrabrominated Lead Naphthalocyanine for Optical Power Limiting

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Abstract: The complex 2,(3)-tetrabromo-3,(2)-tetra[(3,5-di-*tert*-butyl)phenyloxy]-naphthalocyaninato lead [$Br_4(tBu_2C_6H_3O)_4NcPb$, **1**] has been prepared and its optical limiting properties for ns light pulses have been measured. Complex **1** behaves as a reverse saturable absorber within the spectral range 440–720 nm with a limiting threshold of 0.1 $J\,cm^{-2}$ at 532 nm. The lifetime of the absorbing triplet excited state has been evaluated as 3.8×10^{-7} s and the quantum yield of triplet formation has been measured as 0.07 in toluene. The nonlinear optical transmission properties of complex **1** have also been determined in Plexiglas [naphthalocyanine content: 5.0×10^{-4} M (0.1 % by weight)]. A reversible nonlinear absorption was again observed for a fluence above 0.4 $J\,cm^{-2}$, but through different excited-state dynamics. This may be rationalized in terms of aggregation of the molecule in the polymer matrix.

Keywords: lead · naphthalocyanines · nonlinear optics · optical power limiting · transient spectroscopy

Introduction

Among metallophthalo- and metallonaphthalocyanines,[1] complexes of lead[2] and indium[3] are better known examples for displaying strong optical nonlinearities, such as reverse saturable absorption (RSA)[4] of pulsed radiation in the mid-visible range. Such a nonlinear optical (NLO) effect stems from a reversible increase in the effective absorption coefficient of an optical system upon increasing the intensity of the incident radiation. In phthalocyanines (Pcs) and naphthalocyanines (Ncs), RSA takes place through a process of sequential multiphoton absorptions,[5] which generate excited states with larger absorption cross-sections in comparison to that of the parent ground state at the excitation wavelength (λ). To achieve RSA, such excited states must possess lifetimes longer than the duration of the light pulse (typically in the range 10^{-9}–10^{-6} s).[6] For Pc/Nc, this further results in a variance of the transmittance (T_λ) at $\lambda(T_\lambda)$ with the incident light intensity (I_{in}), giving rise to a sigmoid-like profile (see Figure S1 in the Supporting Information).[1b] In the case of Pb and In complexes, the RSA of ns pulses is particularly effective since the heavy-atom effect[2d,7] produced by these heavy central metals accelerates the step of intersystem crossing (ISC), and possibly increases the quantum yield of formation of excited triplet states[8] capable of second photon absorption.[6] The fast and reversible RSA of lead and indium Pcs/Ncs[3a,9,10] can be successfully employed in the construction of optical power limiting (OPL) devices[11] with smart,[3l,12] passive, or self-activated features.[6a,13] In our extensive search for new Pc/Nc-based structures with improved nonlinear transmission (NLT) and OPL properties,[2j,3b–l,12,14,15] we have widely exploited the versatility of the synthetic chemistry of Pcs/Ncs by varying the extent of electronic conjugation of the macrocycle as well as the nature of the central atoms, axial ligands, and peripheral substituents of the designed complexes.[16] In the work described herein, we have prepared 2,(3)-tetrabromo-3,(2)-tetra[(3,5-di-*tert*-butyl)phenyloxy]naphthalocyaninato lead [$Br_4(tBu_2C_6H_3O)_4NcPb$, **1**] (Figure 1) with the aim of characterizing its NLT and OPL properties in liquid solution and in a Plexiglas matrix.

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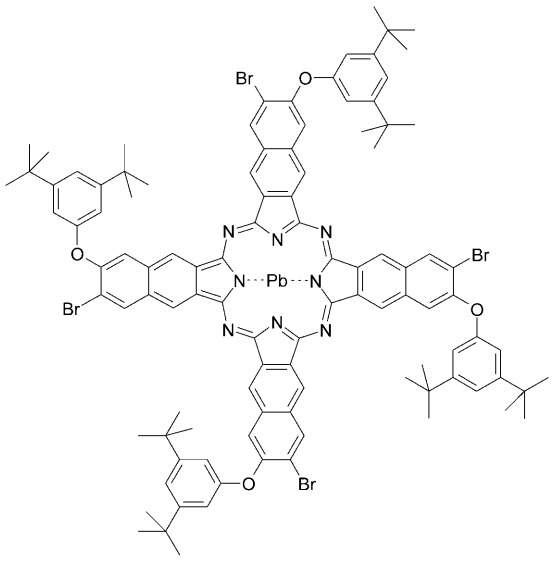

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Figure 1. C_{4v} isomer of lead naphthalocyanine **1** for NLO studies with ns laser pulses.

The motivations for the choice of Pb as central metal, Nc as ligand, and Br and tBu$_2$C$_6$H$_3$O as peripheral substituents in the design of Br$_4$(tBu$_2$C$_6$H$_3$O)$_4$NcPb (**1**) are detailed in the following. The present work has been mainly focussed on the optimization of the molecular structure of an Nc-based system for OPL of ns pulses in the visible spectrum. As far as the limiting of ns laser pulses is concerned, lead phthalo- and naphthalocyaninates[2e] have the advantage of more rapid formation of the strongly absorbing excited state T_1 (usually within 10^{-11} s; see Figure S2 in the Supporting Information) when compared to analogous complexes of lighter central metals.[3i,14d,15] This implies that the initially excited singlet state S_1 (Figure S2) is no longer involved in the limiting action of ns pulses by lead phthalo-/naphthalocyaninates. The dynamics of excited-state formation by pulses of ns duration is therefore considerably simplified in lead complexes when compared to the majority of phthalo-/naphthalocyaninates, the lifetimes of the S_1 states of which are of the order of 1 ns. This is mainly due to the fact that additional transitions between excited singlet states are avoided.[3i,14d,15] In practical terms, the rapid formation of a highly absorbing state of the lead complex corresponds to fast activation of a derived OPL device (within the pulse width), once it senses the stimulus generated by the laser pulse. In addition, lead complexes in the triplet excited state T_1 (see Figure S2 in the Supporting Information) can permit the full absorption of the ns laser pulse since their lifetime τ_{T_1} is usually longer than 10 ns.[2] The recovery time, that is, the time necessary for an excited system to return to the ground state is of the order of a few microseconds for lead phthalo-/naphthalocyaninates,[2] a relatively low value within this class of compounds.[1,3] This indicates that, among metallophthalo- and metallonaphthalocyanines, lead complexes are some of the fastest absorbers for the OPL of ns pulses,[1b] and can sustain irradiation cycles with frequencies as high as 10^3–10^5 Hz in the absence of thermal degradation.

In the analysis of the designed ligand in complex **1**, comparisons were continually made to the analogous phthalocyanines. In comparison to a Pc, the Nc ligand displays a red-shifted Q-band and a concomitant widening of the high transmission window between the B- and Q-bands.[2b,e] This is a direct consequence of the expansion of the network of conjugated π-electrons, which raises the level of the HOMO while leaving the levels of the HOMO−1 and LUMO almost completely unaltered.[17] This change in the ground-state absorption through chemical substitution is also accompanied by a broadening of the region of the visible spectrum over which the Nc ligand possesses an excited-state absorption cross-section, σ_1, larger than that of the ground state, σ_0.[2b,e,3e,14d,18] Moreover, the passage from Pc to Nc does not bring about any shortening of the lifetime τ_{T_1} for the highly absorbing excited triplet state T_1.[2b,e,3e,14d,18] This combination of ground- and excited-state absorption properties renders Ncs particularly attractive with respect to Pcs for OPL devices for ns pulses in the context of eye protection. In fact, in order to achieve a clear field of vision, the eye requires full transmission of light over the whole visible spectrum when the incoming light is of low intensity. In contrast to one based on Ncs, an OPL device based on Pcs would not allow such clarity of vision due to the strong green/blue color of the Pc,[19] which falls in the range of maximum spectral sensitivity of the eye.[20] In addition, the eye needs strong attenuation over a wide spectral range covering the UV/Vis/NIR region when the light intensity exceeds the eye safety threshold (sustainable fluence for the eye is 0.5 μJ cm^{-2} over the UV/Vis/NIR range),[21] in order to prevent permanent damage. In comparison to Pcs, Ncs also permit a better coverage of OPL action above 650 nm.[2b,e,3e,14d,18]

Recently, our group has also developed a new class of conjugated macrocycles based on hemiporphyrazinato (Hps) ligands for OPL devices as alternative materials to Ncs with wide spectral intervals of high transmissivity in the visible range.[22] In contrast to Pcs and Ncs, Hps ligands do not display a Q-band in the Vis/NIR spectrum, and act as OPL materials through a mechanism of simultaneous two-photon absorption from either singlet or triplet excited states.[22] Since the mechanism of nonlinear transmission of ns pulses is dependent on the specific nature of the coordinating central metal in Hps complexes, the structural factors that control and improve the OPL performance of Hps cannot be as straightforwardly assessed as in the case of Ncs.

The choice of Br as peripheral substituent of Nc **1** stems mainly from the observation that brominated Pcs and Ncs possess better OPL properties with respect to the unsubstituted systems.[2i,3d,e,10,14] This has been shown when Br atoms are present either as peripheral substituents on the macrocycle[2i,3d,14] or as axial ligands.[3e,10] Such results can be largely attributed to the internal heavy-atom effect[7] produced by Br when OPL occurs through excited-triplet-state absorption. Besides, it has also been proven that the presence of

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bromide imparts higher photostability and extends the dynamic range of Pcs and Ncs as far as OPL activity is concerned.[2i,3d,14] Similar to fluorinated Ncs[3j,k] and Pcs,[3c] by virtue of its electron-withdrawing character, bromide on Ncs can also induce an increase in the excited-state-absorption cross-section through amplification of the transition dipole moment in the process of excited-state absorption.[3b,c,10d,15] It is also expected that the high electronic polarizability of bromide will favorably affect the extent of absorption by excited states.[3b]

The presence of the four large peripheral 3,5-di-*tert*-butylphenoxy substituents allows the dissolution of Nc **1** in common organic solvents at concentrations as high as 10^{-2} M (the target value for practical use in OPL devices).[3d] Sterically hindering peripheral substituents and a large central metal such as Pb result in a low degree of molecular aggregation, even at high concentrations of Nc **1**. This should prevent the occurrence of strong intermolecular interactions that might deactivate excited states following absorption of the first photon (see Figure S2 in the Supporting Information).[3d,16]

Results and Discussion

UV/visible absorption and emission spectra: The electronic absorption spectrum of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in toluene displays the typical spectral features of a naphthalocyanine, with the characteristic B- and Q-bands[23] appearing at 371 and 826 nm, respectively (Figure 2).

The maximum molar extinction coefficient (ε) (87700 $M^{-1}cm^{-1}$) is observed in correspondence with the Q-band. Vibronic bands with $\varepsilon < 20000\ M^{-1}cm^{-1}$ are also present at shorter wavelengths (730 and 785 nm). The high transmission window of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) lies between 470 and 710 nm. Spectral evidence of molecular aggregation could only be found at concentrations above 1.2×10^{-3} M. The emission and excitation spectra of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in toluene are shown in Figure 3, together with the normalized absorption spectrum.

The emission spectrum of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) displays a characteristic Stokes shift, with the main band at

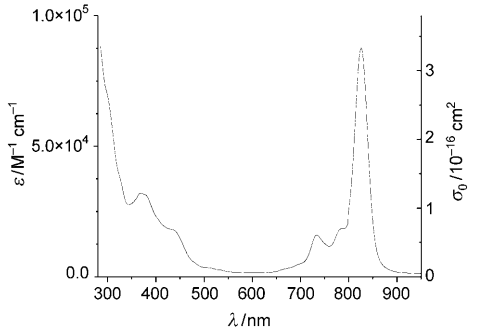

Figure 2. Molar extinction coefficient ε, and linear absorption cross-section σ_0, for $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in the UV/Vis range [C_1: 2.5×10^{-5} M, solvent: toluene].

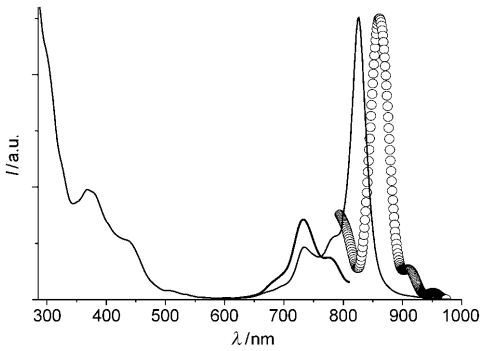

Figure 3. Absorption (black trace), emission (open circles), and excitation (thick black trace) spectra of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in toluene. The emission spectrum has been obtained upon excitation at 734 nm, whereas the excitation spectrum has been obtained by collecting the emission at 861 nm.

861 nm[24] and vibronic structures at higher wavelengths. A lack of any dependence on the presence of oxygen in solution and the small Stokes shift indicate that the observed emission is due to fluorescence and not phosphorescence.[10d] The excitation spectrum of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) has been determined at the wavelength of maximum emission of 861 nm (Figure 3), and features peaks corresponding to those in the absorption spectrum.

Nonlinear optical transmission: Figure 4 shows the variation of the transmittance of a solution of complex **1** in toluene (C_1: 2.8×10^{-4} M; cell thickness: 2 mm) with the incident fluence (the average duration of laser pulses at 532 nm was 9 ns). The transmittance profiles reveal the occurrence of reverse saturable absorption (RSA). The limiting threshold, F_{lim}, that is, the fluence at which the transmittance is half of the linear transmittance,[25] is 0.1 J cm^{-2}. This value is comparable to those of indium phthalo- and naphthalocyanines with heavy axial ligands such as bromide or iodide, but smaller than those of silicon naphthalocyanines (see Table 1).[3e] The NLO transmission profile of tetrabrominated lead complex **1** is similar to that of the analogous indium chloride complex $Br_4(tBu_2C_6H_3O)_4NcInCl$[3d] under the same experimental conditions of incident light intensity and linear optical transmittance at the wavelength of irradiation

Table 1. Comparison of the experimental values of triplet quantum yields (Φ_T) and triplet excited-state lifetimes (τ_{T_1}) for various naphthalocyanines in toluene.

Compound	F_{lim}/J cm^{-2}	Φ_T	$\tau_{T_1}/10^{-6}$ s
$(tBu_2C_6H_3O)_8NcInCl$[a]	0.27	0.225	14.4
$(tBu_2C_6H_3O)_8NcInBr$[a]	0.11	0.287	1.7
$(tBu_2C_6H_3O)_8NcInI$[a]	0.08	0.273	1.6
Br_4NcSiR_2[b]	>1	0.100	67.0
Br_8NcSiR_2[b]	>1	0.130	49.0
$NcSiR_2$[b,c]	>1	0.200	42.0
$Br_4(tBu_2C_6H_3O)_4NcInCl$[d]	2.3	>0.25	<15.0
$Br_4(tBu_2C_6H_3O)_4NcPb$[e]	0.10	0.070	0.4

[a] Ref. [3e]. [b] Ref. [10d]. [c] Ref. [30]. [d] Ref. [3d]. [e] This work.

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(Figure 4). Since $Br_4(tBu_2C_6H_3O)_4NcInCl$ represents an optimized system for OPL,[3d] the comparable NLO behavior of the Pb and InCl complexes (Figure 4) indicates that compound **1** should also constitute one of the most effective of OPL compounds.[2j,3b–l,9–11] The small differences between the OPL performances of $Br_4(tBu_2C_6H_3O)_4NcInCl$ and $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) stem from the red-shifted absorption spectrum of the excited triplet state of lead naphthalocyanine **1** (see below)[2b] with respect to that of the analogous indium chloride complex.[3b,d,13] In Figure 4, the profile of NLO transmission for the non-brominated lead complex $(tBu_2C_6H_3O)_8NcPb$ is also presented. The observed higher limiting threshold of $(tBu_2C_6H_3O)_8NcPb$ with respect to that of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) (0.3 vs 0.1 J cm^{-2}) confirms the beneficial effect of peripheral bromide on the resulting OPL properties of the complex.[2i,3d,10]

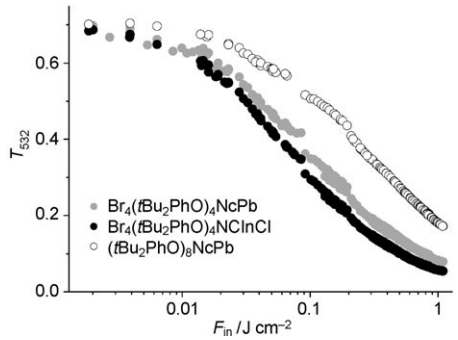

Figure 4. Nonlinear transmittance at 532 nm, T_{532}, for Nc **1** in toluene (C_1: 2.8×10^{-4} M; cuvette thickness: 2 mm). The sample was excited with 9 ns pulses. For comparison, the variations of T_{532} are also shown for 2.3×10^{-4} M $Br_4(tBu_2C_6H_3O)_4NcInCl$[3d] and 7.8×10^{-4} M $(tBu_2C_6H_3O)_8NcPb$.[2j]

As previously discussed,[10d,11a,15,26] the occurrence of efficient RSA has three main implications regarding the nature and the characteristics of the excited state of Nc **1** involved: a) the excited state has a larger absorption cross-section with respect to that of the ground state S_0 at the wavelength of excitation, b) its lifetime τ_{exc} fulfils the condition $\tau_{exc} \geq \tau_p$, where τ_p represents the laser pulse width, and c) the formation time of the excited state is much shorter than the duration of the laser pulse. Since ns pulses are used, the above considerations suggest that, as for analogous Pc- and Nc-based systems,[1–3] RSA originates from one-photon absorption by the optically pumped excited triplet state T_1 (see below for details of the pump and probe experiments). At wavelengths corresponding to the minimum nonlinear transmittance, one can assume that the system is fully converted to the T_1 state (see Figure S2 in the Supporting Information) and absorbs light with an effective one-photon absorption cross-section σ′ given by the relationship:[1b]

$$\sigma^4(\lambda) = \ln[1/T_{min}(\lambda)]/Nl \qquad (1)$$

In Equation (1), N is the concentration of Nc **1** in toluene expressed as molecules cm^{-3}, l is the pathlength through the solution in cm, and T_{min} represents the minimum transmittance that is achieved by the nonlinear absorber. T_{min} corresponds to the transmittance at the end of the sigmoid curve of NLO transmission (see Figure S1 in the Supporting Information). From the experimental data plotted in Figure 4, $\sigma' = 7.43\times10^{-17}$ cm^2 at 532 nm when $T_{min} = 0.08$, $N = 1.7\times10^{17}$ cm^{-3}, and $l = 0.2$ cm. The resulting figure of merit, $\kappa = \sigma'/\sigma_0$, at 532 nm for Nc **1** in toluene solution is 7.4, the ground-state absorption cross-section (σ_0) being 1.02×10^{-17} cm^2 (this corresponds to $\varepsilon = 2670$ M^{-1} cm^{-1}; Figure 2). This value has to be considered as underestimated because the experimental transmittance had not reached its plateau at the minimum value. Comparison with other Ncs displaying $\kappa \leq 5$[3d,e,j,k,10d] shows that tetrabrominated lead complex **1** represents a very efficient multiphoton absorber for OPL purposes within this class of molecular materials.

Transient absorption spectra: The excited state that produces the nonlinear optical response of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) has been characterized by means of pump and probe measurements[3h,27] on a solution of **1** in degassed toluene. Temporal variations of the optical density (ΔOD) at various wavelengths were recorded within 2 μs of the laser pulse (Figure 5).

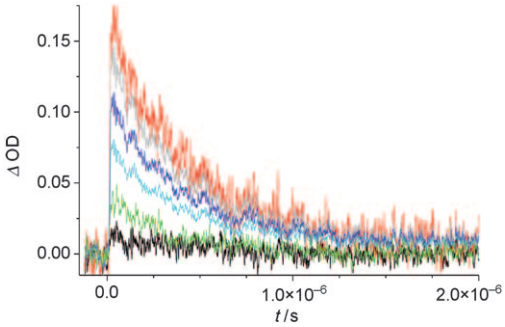

Figure 5. Temporal variations of differential absorbance, ΔOD, at 690 (cyan trace), 680 (blue trace), 660 (grey trace), 630 (red trace), 480 (green trace), and 460 nm (black trace) for Nc **1** in toluene upon excitation at 532 nm with ns pulses (C_1: 2.8×10^{-4} M; F_{in}: 0.13 J cm^{-2}). Profiles are averaged over a series of 150 consecutive traces; $t = 0$ s corresponds to the start time of the laser pulse.

The experiments were carried out at $F_{in} = 0.13$ J cm^{-2}, using the same laser pulses as in the nonlinear transmission experiment (Figure 4). The transient signals in Figure 5 can be fitted by a mono-exponential decay characterized by a time constant of $\tau_{fit} = 0.38$ μs (see Figure 6).

The transient spectra obtained as the difference between the spectrum of the excited state and that of the ground state (Figure 2) at different times from the start of the pulse are shown in Figure 7.

The nature of the excited-state spectrum indicates that it is generated by an excited triplet state of Nc **1** since it features a broad positive band from 440 to 720 nm with a maximum at 630 nm, as found for other Ncs.[6a,b] The positive value of ΔOD shows that the absorbance of the triplet excit-

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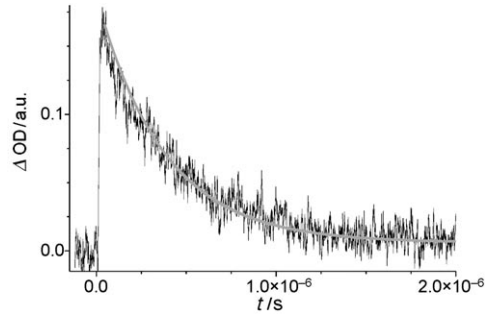

Figure 6. Monoexponential fit (grey line) of differential absorbance ΔOD (black trace) vs time at 630 nm for Nc **1** in toluene. Excitation at 532 nm with 9 ns pulses. The fitted curve was calculated with a mono-exponential decay and a time constant of $\tau_{fit}=0.38$ μs.

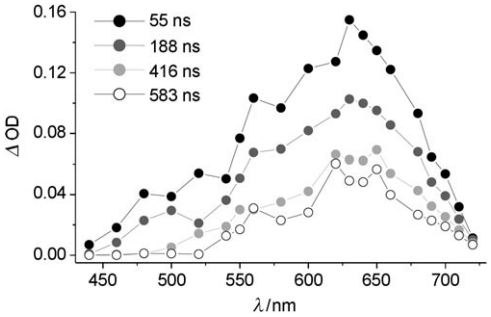

Figure 7. Transient spectra of 2.8×10^{-4} M $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in toluene upon excitation with 9 ns pulses at 532 nm at different times from the start of excitation at $t=0$ s; $F_{in}=0.13$ J cm^{-2}.

ed state is larger than that of the ground state within the examined spectral range, and indicates that RSA for $Br_4(tBu_2C_6H_3O)_4NcPb$ occurs with maximum efficiency at around 630 nm.

Triplet excited-state parameters: The triplet quantum yield of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in toluene at a concentration of 5.5×10^{-5} M was found to be $\Phi_T=0.07\pm0.03$. This value was determined by means of the comparative method[28] with SiNc as the reference compound. The molar extinction coefficient of the triplet state of **1** at 590 nm was measured as $\varepsilon^T(590)=72000\pm4000$ M^{-1}cm^{-1} [$\sigma^T(590)=(2.7\pm0.2)\times10^{-16}$ cm^2] when ZnTPP was used as a triplet donor in the energy-transfer method.[29] The probability of energy transfer was 0.02, the decay time for ^{3}ZnTPP was 5.8×10^{-7} s, and the rate constant for energy transfer between triplet acceptor **1** and triplet donor ZnTPP was 9.5×10^9 M^{-1}s^{-1} at room temperature. Thus, the excited triplet state T_1 of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) is characterized by a relatively low quantum yield of formation ($\Phi_T=0.07$) as well as a short lifetime ($\tau_{T_1}=0.4\times10^{-6}$ s, Figure 6) with respect to other naphthalocyanines (see Table 1).[3e,10d,30]

A decrease of Φ_T upon peripheral bromination of naphthalocyanines has been reported previously for a series of silicon complexes (Table 1),[10d] and a shortening of the excited triplet lifetime in **1** would be expected owing to the presence of five heavy atoms such as Br and Pb, which accelerate the decay of the excited triplet state.[7] Nevertheless, $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) displays remarkable NLO transmission properties at 532 nm for ns laser pulses (Figure 4). In the next section, it is demonstrated that the OPL of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) may be rationalized in terms of its large excited-state absorption cross-section and high rate of excited-state formation (see below).

Kinetic parameters of multiphoton absorption: Pump and probe measurements suggest that the most appropriate kinetic model for the description of the nonlinear optical absorption of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) is sequential two-photon absorption.[4d,e,6a,e] This describes the absorption of a first photon by the ground state (transition $S_0\rightarrow S_1$), followed by the absorption of a second photon by the first excited triplet state T_1 (transition $T_1\rightarrow T_2$) (see Figure S2 in the Supporting Information). Solving of the following kinetic equations confirms this hypothesis.

The dynamics of the ground- and excited-state populations for this model may be described by the following set of differential equations:[3h]

$$\frac{dN_{S0}}{dt}=-\sigma_0N_{S0}I_{in}+\sigma_0N_{S1}I_{in}+\frac{N_{S1}}{\tau_{S1}}+\frac{N_{T1}}{\tau_{T1}} \quad (2a)$$

$$\frac{dN_{S1}}{dt}=\sigma_0N_{S0}I_{in}-\sigma_0N_{S1}I_{in}-\frac{N_{S1}}{\tau_{S1}}-k_{ISC}N_{S1} \quad (2b)$$

$$\frac{dN_{T1}}{dt}=k_{ISC}N_{S1}-\sigma_1N_{T1}I_{in}+\sigma_1N_{T2}I_{in}-\frac{N_{T1}}{\tau_{T1}}+\frac{N_{T2}}{\tau_{T2}} \quad (2c)$$

$$\frac{dN_{T2}}{dt}=\sigma_1N_{T1}I_{in}-\sigma_1N_{T2}I_{in}-\frac{N_{T2}}{\tau_{T2}} \quad (2d)$$

In Equations (2a–d), N_i denotes the population densities in the different i states, k_{ISC} and τ_i denote the intersystem crossing rate and the lifetimes of the excited states (see Figure S2 in the Supporting Information), and I_{in} indicates the incident intensity (in photons cm^{-2} s^{-1}) of the pulses presenting a Gaussian temporal profile and a top hat spatial profile. Fitting the experimental data requires numerical solutions of the rate equations [Eqs. (2a–d)][31] with optimization of the parameters that are not available experimentally, namely k_{ISC}, τ_{S_1}, and τ_{T_2}. Figure 8 shows the fitting curves as T vs $\log(F_{in})$ and F_{out} vs F_{in}, to evidence the quality of the fitting in low-and high-fluence regimes, respectively. The fitting curves in Figure 8 were obtained using the values reported in Table 2. The good fitting and the parameter values confirm the validity of the proposed kinetic model based on sequential two-photon absorption involving triplet states. Additional absorptions starting from the S_1 excited state as well as higher excited triplet states T_n were also considered in the model, but the resulting fittings were generally of much lower quality.

The resulting triplet quantum yield, Φ_T,[7b] calculated with the values in Table 2, is 0.085. This value is within the uncertainty range of that determined experimentally ($\Phi_T=0.07\pm$

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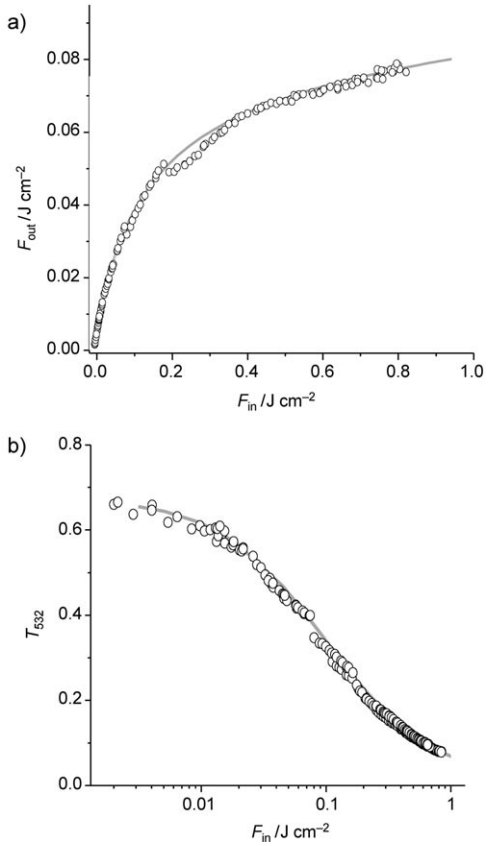

Figure 8. Fitting of a) F_{out} vs F_{in} and b) T_{532} vs F_{in} profiles for $Br_4(t Bu_2C_6H_3O)_4$NcPb (**1**) in toluene upon excitation with 9 ns pulses at 532 nm. Fitting (continuous line) has been obtained with the multiphoton absorption model depicted in Figure S1 using the parameter values reported in Table 2 (see below).

Table 2. Values of optimized (τ_{S_1}, k_{ISC}, τ_{T_2}) and experimental (σ_0, τ_{T_1}, σ_1) parameters used for the fitting of the nonlinear transmission data of $Br_4(t Bu_2C_6H_3O)_4$NcPb (**1**) in toluene (Figure 8).

Parameter	Value
σ_0 [cm^2]	1.02×10^{-17}
τ_{S_1} [s]	5.00×10^{-12}
k_{ISC} [s^{-1}]	1.86×10^{10}
τ_{T_1} [s]	0.38×10^{-6}
σ_1 [cm^2]	2.67×10^{-16}
τ_{T_2}[s]	1.00×10^{-13}

0.03) through the comparative method.[28,30,32] It can also be observed that, as expected, the figure of merit, $\kappa = 26.2$, obtained with the data shown in Table 2, is higher than that obtained above [Eq. (1)]. In spite of the low ISC, the overall dynamics of the excited states allows a sufficient level of accumulation of the population of the triplet state, which, given its high absorption cross-section, allows good OPL performance for the present molecule. The particular dynamic found for Nc **1** is characterized by very fast ISC. This is a very encouraging result with regard to the construction of an OPL device exhibiting a fast response.

Photophysical properties of $Br_4(t Bu_2C_6H_3O)_4$NcPb incorporated in Plexiglas: Molecular materials in solid or polymeric matrices can retain the nonlinear optical properties of their liquid solutions, as previously demonstrated for Pcs and Ncs dispersed in optical polymers such as polystyrene, polycarbonate or poly(methyl methacrylate) (PMMA).[3a,l,6c,15,33] This fact has considerable importance for the practical realization of passive OPL devices.[3l,6a,b,9,11,34] We prepared a polymeric sample of good optical quality by dispersing $Br_4(t Bu_2C_6H_3O)_4$NcPb (**1**) in Plexiglas. The sample was prepared by extrusion, with a concentration of **1** of 0.1% by weight. This corresponds to a molar concentration of 5.0×10^{-4} M with respect to the volume of Plexiglas. This extrusive method was found to be more appropriate for obtaining samples of high optical quality in comparison to other known processes, such as co-dissolution of the polymer and the molecule in a common solvent followed by spin-coating or casting.[3l,35] The optical spectrum of $Br_4(t Bu_2C_6H_3O)_4$NcPb (**1**) in the obtained sample of Plexiglas film (thickness: 1.7 mm) is shown in Figure 9.

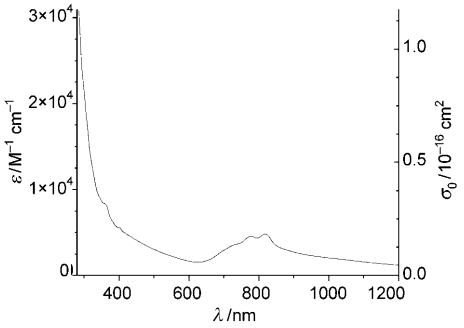

Figure 9. Molar extinction coefficient, ε, and linear absorption cross-section, σ_0, for $Br_4(t Bu_2C_6H_3O)_4$NcPb (**1**) in Plexiglas [C_1: 5.0×10^{-4} M; film thickness: 1.7 mm].

The lower values of molar extinction coefficient for $Br_4(t Bu_2C_6H_3O)_4$NcPb (**1**) in Plexiglas ($\varepsilon < 7\times10^3$ M^{-1}cm^{-1} for $\lambda > 400$ nm; Figure 9) with respect to its solution in toluene (Figure 2) reflect a high extent of molecular aggregation in the polymeric sample.[3b,d,m,36] Irradiation of the sample with 9 ns pulses at 532 nm resulted in variations in the optical transmission, which are presented in Figure 10. The optical response of Plexiglas under the same irradiation conditions is also shown in Figure 10. The latter experiment was carried out to evaluate possible contributions to the optical nonlinearities of the sample derived from the polymeric matrix itself.[35]

$Br_4(t Bu_2C_6H_3O)_4$NcPb (**1**) in Plexiglas gives rise to RSA[4] within the incident fluence range $0.07 \le F_{in} \le 0.4$ J cm^{-2} (Figure 10). It can be seen that within this range of nonlinear optical activity, the Plexiglas matrix did not show any relevant modification of its optical transmission. However, opaque spots with a milky appearance were formed in correspondence with the irradiated area when $F_{in} > 0.4$ J cm^{-2}, with a consequent irreversible decrease in transmittance.

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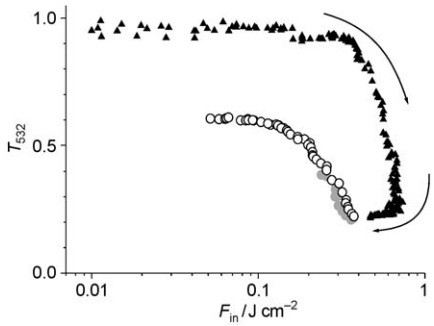

Figure 10. Nonlinear transmittance at 532 nm, T_{532}, for Plexiglas (▲), and $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) (○,●) in Plexiglas [C_1: 5.0×10^{-4} M; film thickness: 1.7 mm]. Polymeric samples were excited with 9 ns pulses at 532 nm. Grey filled circles refer to the variations of T_{532} for **1** in Plexiglas upon diminution of the incident fluence F_{in}. Arrows indicate the direction of variation for F_{in} during the irradiation of Plexiglas alone.

This effect was probably due to polymer modification induced by the absorption of optical energy by the Nc. Comparison of the normalized transmittance curves of Nc **1** in toluene and Plexiglas (Figure 11) reveals striking differences in the excited-state dynamics.

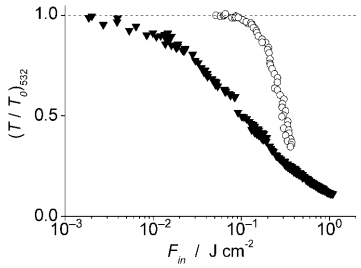

Figure 11. Variations of normalized transmittance at 532 nm for $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in toluene (▼) and Plexiglas (○). Linear transmittance values at 532 nm are 0.70 and 0.60 when **1** is dispersed in toluene and Plexiglas, respectively.

The onset of nonlinear optical behavior occurs at much lower fluences for the toluene sample as compared to the Plexiglas sample (4×10^{-3} vs 7×10^{-2} J cm^{-2}). Moreover, once the nonlinear optical regime is reached, the decrease in nonlinear transmission is much steeper when the complex is dispersed in the polymeric matrix (Figure 11). The observed differences in the dynamics of the excited states can be attributed to the intermolecular aggregation in the polymeric sample, which generates additional relaxation channels for excited **1**, as well as the polymeric environment, which unavoidably influences the dynamics of the formation/relaxation of excited states of the embedded molecules. This situation may lead to the activation of higher order nonlinear processes in the polymeric sample, with the absorption of more than two photons at higher fluences. This can be deduced from the steeper decrease in the transmittance of **1** in the polymeric sample once the nonlinear regime is reached.[22] The observed behavior shows that better control of the aggregation must be pursued if one also wants to exploit the nonlinear absorption properties of $Br_4(tBu_2C_6H_3O)_4NcPb$ (**1**) in a polymer matrix at low values of incident fluence.

Conclusions

The tetrabrominated lead complex 2,(3)-tetrabromo-3,(2)-tetra[(3,5-di-*tert*-butyl)phenyloxy]naphthalocyaninato lead (**1**) has been prepared and studied for optical power limiting purposes. The design of the structure of complex **1** has been mainly driven by the intention of increasing the rate of intersystem crossing for fast population of the first triplet excited state. This has been made possible through the addition of heavy atoms (four bromide substituents) at the periphery of the macrocycle and the insertion of a heavy atom (lead) in the central cavity of the ligand. These structural choices were motivated by the recognition of high intersystem crossing rate and efficient population of the first excited triplet state as the most crucial factors for the improvement of the optical power limiting effect through a mechanism of excited-triplet-state absorption. Lead naphthalocyanine **1** behaves as a reverse saturable absorber of ns pulses in the broad spectral range 440–720 nm. At 532 nm, complex **1** in toluene displays a limiting threshold of 0.1 J cm^{-2} when its linear transmission is 0.70. The excited triplet state that accounts for the observed nonlinearities has a lifetime of about 0.4 μs. The triplet quantum yield of naphthalocyanine **1** was found to be 0.07, and the triplet formation rate was particularly high (of the order of 10^{11} s^{-1}). The effect of the low ISC yield was overwhelmed by the fast dynamics of excited-state formation, rendering Nc **1** particularly interesting for fast devices. Therefore, it is concluded that the fast dynamics and large absorption cross-section of the triplet state are critical for the manifestation of the more attractive optical limiting performance of Nc **1** compared to that of analogous compounds. The nonlinear transmission profile of naphthalocyanine **1** at 532 nm has been fitted with a model of sequential two-photon absorption. The nonlinear transmission properties of complex **1** at 532 nm were also determined when the system was dispersed in Plexiglas through an extrusion process. The dynamics of excited-state formation of **1** in Plexiglas was found to be considerably different from that in toluene solution. This can be rationalized in terms of possible molecular aggregation within the polymeric sample.

Experimental Section

Synthesis of $Br_4(tBu_2C_6H_3O)_4NcPb$ (1): 6-Bromo-7-[(3,5-di-*tert*-butyl)-phenoxy]-2,3-dicyanonaphthalene[2j,3d,17] (1.4 g, 3 mmol) was heated in 1-chloronaphthalene (1 mL) at 140 °C. Lead(II) acetate (325 mg, 1 mmol) was then added and the solution was heated to 195 °C for 4.5 h. After cooling, the mixture was poured into methanol (100 mL) and stirred. The precipitate that formed was collected and washed several times with hot methanol. Nc **1** was obtained as a dark yellow-brownish powder (500 mg,

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57%). ^{1}H NMR (250 MHz, [D$_8$]THF, 25°C, TMS): $\delta = 1.33$ (s, 72H), 7.06/7.39 (m, 12H), 8.17/8.28 (m, 8H), 9.19–9.40 ppm (m, 8H); ^{13}C NMR (250 MHz, [D$_8$]THF, 25°C, TMS): $\delta = 30.7$, 34.9, 114.6, 118.9, 134.2, 136.6, 153.3, 155.8 ppm; MS (FAB): *m/z*: calcd for $C_{104}H_{100}N_8O_4Br_4Pb$: 2052.8 Da; found: 2054.8 [M^+]; elemental analysis calcd (%) for $C_{104}H_{100}N_8O_4Br_4Pb$: C 60.85, H 4.91, N 5.46; found: C 61.4, H 4.7, N 6.0.

Preparation of polymeric samples: Inclusion of $Br_4(t Bu_2C_6H_3O)_4NcPb$ (**1**) in Plexiglas 6N type was accomplished by extrusion at 220–260°C using a Haake Minilab apparatus. At the operational temperatures adopted, naphthalocyanines do not undergo decomposition. Extruded samples were disc-shaped and after fine polishing had a final thickness of 1.5–2.0 mm. In the polymeric samples prepared by extrusion, Nc **1** was homogeneously dispersed at a concentration of 5.0×10^{-4} M (0.1% by weight).

Spectroscopic measurements: Optical absorption spectra of $Br_4(t Bu_2C_6H_3O)_4NcPb$ (**1**) in deaerated toluene and in a Plexiglas matrix were recorded with a Varian Cary 5 UV/Vis/NIR spectrophotometer. Fluorescence and excitation spectra of Nc **1** in degassed toluene solution were obtained with a Perkin–Elmer LS-50 B spectrometer.

Nonlinear transmission measurements: Nonlinear transmittance of Nc **1** was recorded at 532 nm using 9 ns pulses of a doubled Nd:YAG laser (Quantel YG980E). Transmitted energies were measured with a pyroelectric detector (Scientech SPHD25) and results were obtained as an average of ten measurements at 1 Hz in the open-aperture configuration. The intensities of the incident pulses were controlled through a combination of a $\lambda/2$ wave-plate with a polarizing cube beam-splitter. Cells with an optical pathlength of 2 mm were used and the illuminated spot on the sample was about 0.025 cm^2. The analysis of the nonlinear transmission data is based on the model presented in Figure S1, and the kinetic equations for the dynamics of the excited states corresponding to the model were solved numerically.[31]

Pump and probe experiments: The transient excited-state spectra of $Br_4(t Bu_2C_6H_3O)_4NcPb$ (**1**) were determined by means of the pump and probe technique.[3h,27] In these experiments, the sample was excited with the same pulses as used for the measurements of nonlinear transmission at a frequency of 5 Hz. The fluence of excitation was 0.12 J cm^{-2} per pulse. The excited-state absorption of Nc **1** was probed using the white light generated by a stabilized 150 W Xe lamp. The temporal variations of nonlinear optical absorption were recorded with a 1 GHz digital oscilloscope (LeCroy LC564A). An average was obtained from 100 signals in order to ensure a high signal-to-noise ratio. Differential transient spectra of $Br_4(t Bu_2C_6H_3O)_4NcPb$ (**1**) were obtained at different delay times with respect to the laser pulse using the transient signals. A Jobin–Yvon Horiba TRIAX 320 spectrometer, equipped with 600 and 300 groove mm^{-1} gratings, and a Hamamatsu R2257 phototube with a rise time of 2.6 ns were used to record the probe signal.

Determination of triplet parameters: The triplet quantum yield, Φ_T, of $Br_4(t Bu_2C_6H_3O)_4NcPb$ (**1**) in degassed toluene was determined by means of the comparative method[28] using silicon naphthalocyanine (SiNc)[30] and zinc tetraphenylporphyrin (ZnTPP)[32] as standards with known values of triplet quantum yield Φ_S (0.20 for SiNc, 0.83 for ZnTPP) and triplet-triplet extinction coefficients, ε^S, at specific wavelengths (70000 M^{-1} cm^{-1} for SiNc at 590 nm,[30] 73000 M^{-1} cm^{-1} for ZnTPP at 470 nm).[32] The extinction coefficient of the triplet-to-triplet transition of **1**, needed for the comparative method, was obtained by the energy-transfer method[29,30] using the experimental determination of the probability of energy transfer.[29b]

Acknowledgements

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