Nonlinear optical effects related to saturable and reverse saturable absorption by subphthalocyanines at 532 nm†

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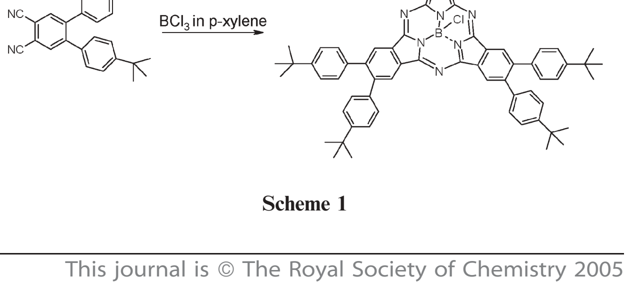
It is found that both effects of saturable absorption and reverse saturable absorption are obtained with a solution of subphthalocyanine 2 at 532 nm depending on the intensity of 9 ns laser pulses; saturable absorption occurs at lower intensity levels whereas the reverse effect prevails at higher levels; contrary to expectations, subphthalocyanines can behave as reverse saturable absorbers at 532 nm, despite the high linear absorption at this wavelength; data have been fitted with a five-level model which considers three consecutive electronic transitions with absorption cross-section values of 1.4×10^{-16}, 1.0×10^{-16} and 40×10^{-16} cm^2, respectively.

Subphthalocyanines (SubPcs)[1] are conjugated complexes possessing special nonlinear optical (NLO) properties due to the simultaneous presence of an aromatic electronic structure,[2] nonplanar skeleton[3] and a multipolar distribution of electrical charge.[4] Despite the many studies on the second- and third-order NLO properties of SubPcs no evidence of their optical limiting (OL)[5] properties for ns pulses at 532 nm or any other wavelength in the visible has been reported so far. Different to SubPcs, phthalocyanines (Pcs) and naphthalocyanines (Ncs) are very well known for their remarkably strong OL of ns pulses in the visible range.[6] This is due to their enhanced excited triplet state absorption,[6] which generates the NLO effect of reverse saturable absorption (RSA).[7] In the case of SubPcs the effect of RSA could be produced at 532 nm if these afford excited electronic states with particularly high absorption cross-sections at this wavelength, say larger than 1×10^{-16} cm^2, since SubPcs generally display high linear absorption at 532 nm[4b] (see Fig. 2 below). On the other hand, the presence of a non-heavy central atom such as boron, and the bright fluorescence in the visible, are features that do not favor effective ISC in excited SubPcs.[8a] Consequently, the excited triplet state of SubPcs would be populated with moderate yields and excited triplet state absorption would thus be comparatively weak.[6,9] On the other hand, replacement of the axial ligand coordinated by central boron of SubPcs[10] with heavy atoms leads to an increase of the rate and yield of ISC.[4b] Despite the moderate yields of triplet state formation in SubPcs the lifetime of their excited triplet state is long enough[4b] to allow the facile absorption of short-pulsed radiations such as in the ns range. In particular, long-living excited states can be generated in SubPcs because of their generally high solubility which diminishes the probability of formation of molecular aggregates and, consequently, decreases the rate of relaxation of excited states.[6c,11,12] Another advantage of highly soluble systems is the possibility of reaching high concentrations of absorber[6c,d] in the excited state with consequent generation of stronger optical effects.[13] In fact, the systems under investigation for OL studies are concentrated solutions of the photoactive molecular material[6c,d] in order to maximize the NLO effect[13] associated with such a material. In SubPcs high solubility is warranted by the cone-shaped structure of the ligand[1] and the possible presence of bulky peripheral substituents[1,4] such as *p-tert*-butylphenyl,[14] *m*-trifluoromethylphenyl,[14b] or *m*-trifluoromethylphenyloxy.[14b] For this reason we synthesized hexa(*p-tert*-butylphenyl)subphthalocyaninato boron chloride and hexa(*m*-trifluoromethylphenyl)subphthalocyaninato boron chloride for OL studies [$(t\mathrm{BuPh})_6$SubPcBCl and $(\mathrm{CF_3Ph})_6$SubPcBCl in Schemes 1 and 2, respectively). These SubPcs, unlike the unsubstituted one, are sufficiently soluble to permit the acquisition of their ^{13}C NMR spectra.[1,4] The first phenyl substituted $(t\mathrm{BuPh})_6$SubPcBCl was synthesized from 4,5-bis(*p-tert*-butylphenyl)phthalonitrile and $\mathrm{BCl_3}$ (Scheme 1). However, the resulting SubPc displayed poor photostability and the NLO properties could not be determined for $(t\mathrm{BuPh})_6$SubPcBCl. To increase the photostability of a system the addition of substituents with electron-withdrawing (EW) character such as F,[15] $\mathrm{CF_3}$[15a] and *m*-trifluoromethylphenyl is necessary.[16] We attempted the synthesis of $(\mathrm{CF_3Ph})_6$SubPcBCl through the reaction of the corresponding phthalonitrile **1**[14b] with $\mathrm{BCl_3}$ in *p*-xylene at 150 °C (Scheme 2).[17] Elemental analysis (EA), ^{1}H, ^{13}C NMR and MALDI-TOF mass spectrometry revealed that product **2** (Scheme 2) is actually constituted by a mixture of SubPcs with general formula $(\mathrm{CF}_{3-x}\mathrm{Cl}_x\mathrm{Ph})_6$SubPcBCl, in which the target compound $(\mathrm{CF_3Ph})_6$SubPcBCl with $x = 0$ in **2** is the most abundant



Scheme 1

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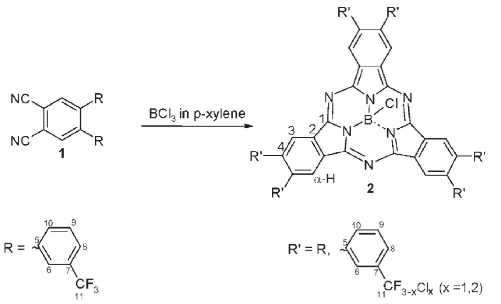

Scheme 2

(see ESI†). Different to (tBuPh)$_6$SubPcBCl, SubPcs **2** with peripheral EW substituents, displayed enhanced photostability both in solution and in the solid state. This prompted us to evaluate the OL properties[9b,18] of **2** at 532 nm since the verification of such a NLO effect requires the interaction of photochemically stable materials with high intensity radiations (in the order of 10^{10} W m^{-2}), such as those produced by pulsed lasers.[19] Figs. 1 and 2 show the nonlinear transmitted intensity I_{out} at 532 nm and the linear absorption spectrum of a solution of **2** in toluene, respectively. Laser pulses with 9 ns time duration and a repetition rate of 2 Hz were used for the NLO measurements. This repetition rate is sufficiently low to avoid sample overheating and accumulating effects due to the possible slow relaxation processes of SubPcs excited states. The nonlinear variation (Fig. 3) of the optical transmission of **2** at 532 nm *vs.* the incident intensity is obtained directly from the ratio $I_{\mathrm{out}}/I_{\mathrm{in}}$ (Fig. 1). The transmission is reported against input intensities on a logarithmic scale to give evidence to the data at low incident intensities which would not be otherwise appreciated from Fig. 1. Fig. 3 indicates that $(\mathrm{CF}_{3-x}\mathrm{Cl}_x\mathrm{Ph})_6$SubPcBCl **2** displays both effects of saturable absorption (SA) and RSA.[20] SA at 532 nm occurs below about 3×10^{25} photons cm^{-2} s^{-1}, *i.e.* below 1.12×10^{11} W m^{-2}, as indicated by the initial increase of transmittance with respect to the linear value ($T_0 = 0.56$). For values of incident intensity higher than 4×10^{25} photons cm^{-2} s^{-1} SubPcs **2** start to behave as a reverse saturable absorber since transmittance decreases continuously until a minimum value of 0.32. The present case is not the first one in which the same absorber displays both SA and RSA depending on the input intensity.[20] However, it is remarkable that SubPcs **2** could display also RSA at the present wavelength of analysis since linear absorption is very high (linear absorption cross-section σ_S for **2** is 1.4×10^{-16} cm^2 at 532 nm from Fig. 2). Preliminary results on $(\mathrm{CF_3PhO})_6$SubPcBBr (not reported here) also show an analogous NLO behavior in terms of the variation of the transmitted energy with the incident energy of ns pulses at 532 nm.

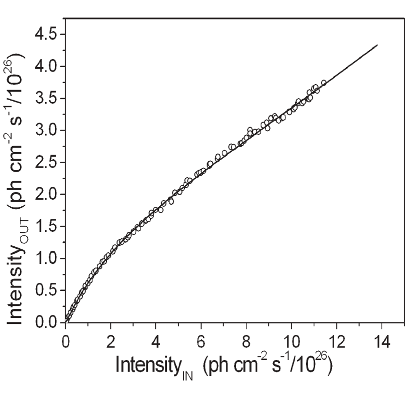

Fig. 1 Transmitted intensity *vs.* incident intensity at 532 nm for 3.5×10^{-5} M $(\mathrm{CF}_{3-x}\mathrm{Cl}_x\mathrm{Ph})$6SubPcBCl (**2**) solution in toluene. Cuvette thickness: 2 mm. The ratio $I_{\mathrm{out}}/I_{\mathrm{in}}$ of the data of this figure corresponds to the NLO transmittance shown in Fig. 3 (see below). The continuous curve is the result of a calculation with the five level model (see text).

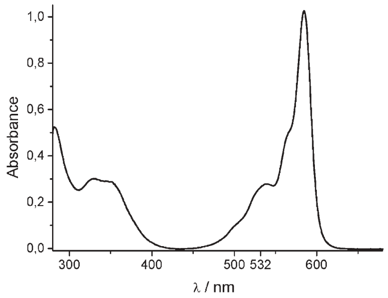

Fig. 2 Linear optical spectrum of 3.5×10^{-5} M $(\mathrm{CF}_{3-x}\mathrm{Cl}_x\mathrm{Ph})_6$-SubPcBCl (**2**) solution in toluene. Cuvette thickness is the same as for the plot in Fig. 1.

A model which is able to account for the presented experimental data has to consider first that a strong absorption takes place at the pumping frequency (532 nm) and that SA is obtained when higher energy levels absorb less effectively than the ground state. Since it is known that ISC is active for these molecular systems, and that the first singlet excited state lifetime is comparatively short with respect to ns pulses,[21] we have initially considered the presence of only one triplet state (four-level model).[8b] A calculation of the variation of the optical transmission through this model could be done on the basis of the population dynamics of ground and excited states.[22] Solution of the kinetic equations was obtained according to Ehlert *et al.*[23] (see ESI†) using a top-hat profile for the laser pulses, which is very similar to what is produced in correspondence of the focus in the actual laser beam. Fig. 3 shows

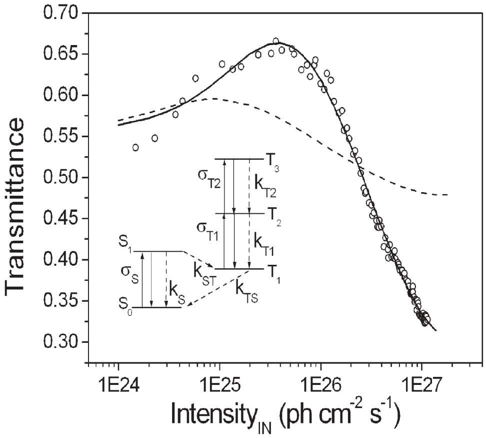

Fig. 3 Optical transmittance of 3.5×10^{-5} M $(\mathrm{CF}_{3-x}\mathrm{Cl}_x\mathrm{Ph})_6$SubPcBCl (**2**) solution in toluene with incident intensity at 532 nm. Errors of the transmittance values are estimated to be of the order of 0.1 at very low intensities, but 0.02 at intermediate intensities and 0.01 at higher intensities. The continuous curve is the result of a calculation based on the model shown in the inset, whereas the dashed curve refers to the same model but without the T$_3$ level (see text).

the result of this type of calculation (dashed line). Although the modelled RSA starts at lower intensities than in the experiment, the calculation completely fails to reproduce the fast decreasing transmittance at higher intensities. The involvement of an excited singlet level for upper absorption did not produce a better fitting. We found that the simpler model which accounts for the experimental data has to consider an additional level in the triplet manifold (five-level model) (see inset of Fig. 3). The calculation based on the five-level model gives a good fitting of the experimental data at both low (Fig. 3), and higher intensities (Fig. 1).[24] The model considers three consecutive transitions, and the best fitting is obtained when the absorption cross-sections values are $\sigma_S = 1.4 \times 10^{-16}$, $\sigma_{T1} = 1.0 \times 10^{-16}$ and $\sigma_{T2} = 40 \times 10^{-16}$ cm^2. Only σ_S has been experimentally determined from the linear optical spectrum (Fig. 2), whereas the other parameters have been obtained from the fitting. Rate constants of the reported fitting are $k_S = 6.5 \times 10^9$ s^{-1}; $k_{ST} = 0.25 \times 10^9$ s^{-1}; $k_{T1} = 1.95 \times 10^{11}$ s^{-1}; $k_{T2} = 3 \times 10^{12}$ s^{-1} and $k_{TS} = 1.0 \times 10^5$ s^{-1}. As expected for this type of complexes, k_S and k_{ST} are comparable. Therefore, the RSA behaviour of SubPcs **2** is due to 1 + 1 photon absorption from an excited state as recently observed in other systems.[25]

Despite the high likelihood of the proposed model, further refinements can be brought, considering additional data (not available yet) from pump and probe experiments in the ps and ns time scales.

In conclusion, we have demonstrated for the first time that SubPcs can display at 532 nm both NLO effects of SA and RSA. In particular, the NLO transmission of the photostable system $(CF_{3-x}Cl_xPh)_6$SubPcBCl (**2**) has been determined at 532 nm with ns laser pulses. A five-level model has been proposed for the analysis of the multiphoton absorption properties of **2**, and this gave a good fitting of the experimental data at both low and high input intensities when the absorption cross-sections σ_S, σ_{T1} and σ_{T2} for the three consecutive transitions $S_0 \rightarrow S_1$, $T_1 \rightarrow T_2$ and $T_2 \rightarrow T_3$ were related by the relationship $\sigma_{T1} < \sigma_S < \sigma_{T2}$.

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