Inorganica Chimica Acta 363 (2010) 3945–3950

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and high ranked NLT properties of new sulfonamide-substituted indium phthalocyanines

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ARTICLE INFO

Article history:
Received 26 January 2010
Received in revised form 14 July 2010
Accepted 20 July 2010
Available online 27 July 2010

Keywords:
Phthalocyanines
Sulfonamides
Nonlinear optics

ABSTRACT

The synthesis and characterization of three new indium phthalocyanines bearing eight *N*-alkyl- or *N*-aryl-sulfonamide groups is described. The new compounds are {2,3,9,10,16,17,23,24-octakis[4-(4-methoxyphenylaminosulfonyl]phenoxy]phthalocyaninato}indium(III) chloride (**7**), {2,3,9,10,16,17,23,24-octakis[4-diethylaminosulfonyl)phenoxy]phthalocyaninato}indium(III) chloride (**8**) and {2,3,9,10,16,17,23,24-octakis[4-didodecylaminosulfonyl)phenoxy]phthalocyaninato}indium(III) chloride (**9**), and were obtained in 23–49% yields. The precursors of phthalocyanines **7**–**9** are sulfonamide-substituted phthalonitriles that can be prepared by reacting 4,5-bis(4-chlorosulfonylphenoxy)phthalonitrile (**3**) with amines. The nonlinear transmission (NLT) of complexes **7**–**9** was determined at 532 nm using ns pulses. All three phthalocyanines behave as reverse saturable absorbers with increasing efficiency of optical limiting in the order **7** < **8** < **9**. A comparative analysis of the NLT results is attempted in terms of the structural differences in **7**–**9**.

1. Introduction

Peripheral modulation of macrocyclic compounds is a challengeable and attractive pathway in the search for new materials. In this respect, peripheral modification of phthalocyanines is still a rewarding route to new materials suitable for diverse applications.

Due to their properties, phthalocyanines have a vast area of applications [1], namely as dyes [2], catalysts [3,4], chemical sensors [5–8] and as sensitizers in photodynamic therapy of several diseases [9–13]. Other interesting applications are related with their nonlinear transmission (NLT) properties [14–18], for instance the limiting of laser radiation intensity. This is due to their large nonlinearities, intrinsic fast response time, broadband spectral response and processing straightforwardness. Optical limiters, whose filtering action is instantaneously activated by the incoming intense light, represent a valid solution for the protection of sensors. In this case, the incoming intense light alters the absorptive and refractive properties of the materials in such a way that the resulting transmitted intensity is greatly reduced. Optical limiters based on reverse saturable absorption (RSA) are transparent to weak light and get opaque to intense light. Moreover, if only RSA occurs, the quality of the vision can still be maintained during the process of optical limiting (OL).

Occurrence of RSA via the mechanism of excited-state absorption in Pcs has inspired several studies with the aim of establishing systematic correlations between the Pc structure and the corresponding value of excited-state absorption cross section at the wavelength of analysis [14–18]. In doing so, Pcs and analogues have found a prominent place as active materials for the important application of optical limiting in the passive self-activated mode [19–22].

The reason for the large employment of Pcs in OL is related with the possibility of varying their electronic configurations in a controlled fashion through peripheral substitution, variation of the central atom, or modification of the axial ligand [23,24]. These characteristics of Pcs and analogues derive from the possibility of forming electronic excited states with a sufficiently long lifetime to afford the successive efficient absorption of photons under short pulsed irradiation (usually, in the ps or ns range) [18]. When excited-state absorption occurs from a triplet excited state the related OL effect can be further improved in Pcs through the coordination of heavy central atoms, e.g. Pb [25] or In [26–38], which accelerate intersystem crossing (ISC) by means of spin–orbit coupling in the excited complex.

One disadvantage of unsubstituted phthalocyanines is their extreme insolubility in most organic solvents, due mainly to the highly planar and aromatic core. Peripheral functionalization of a

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doi:10.1016/j.ica.2010.07.062

phthalocyanine with appropriate groups can afford new derivatives with increased solubility in apolar or polar organic solvents or even in aqueous media. Sulfonated phthalocyanines, both in the sulfonato and sulfonamide forms, are already described in the literature [39,40]. Some of these compounds show potential application in photodynamic therapy [11–13] or in the production of other materials, due to their interesting photoconductive properties [6].

Electron-withdrawing substituents are known to produce an enhancement on the NLT properties of phthalocyanines [35,36]. Taking this in consideration, we idealized the synthesis of three phthalocyanine derivatives bearing eight sulfonamide groups. The NLT properties of the resulting phthalocyanines were evaluated in order to verify whether these substituents have any pronounced effect and, therefore, if the new compounds could be considered effective materials for NLT.

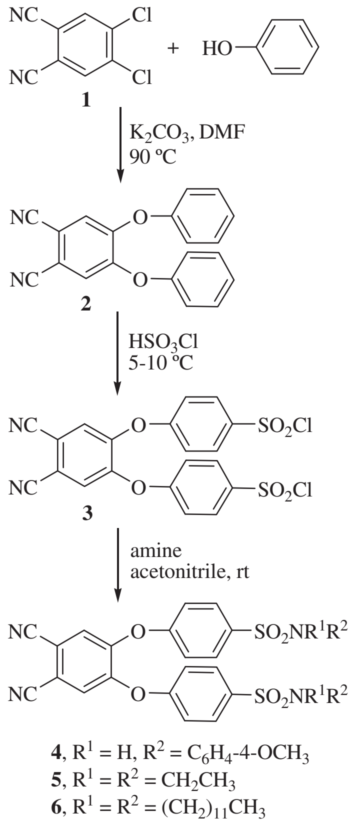
2. Experimental

2.1. Materials and methods

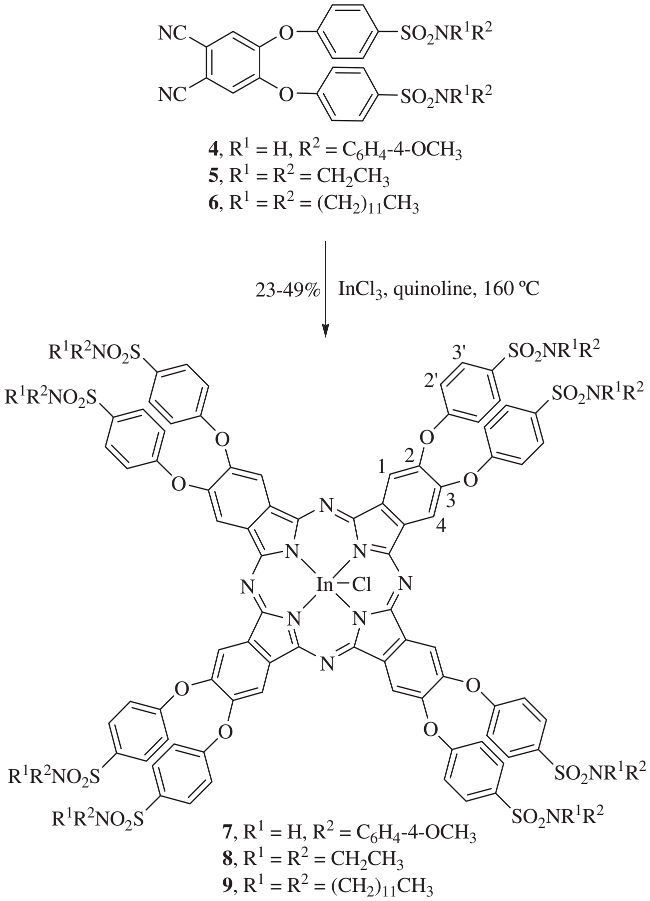
Compounds **2–6** (Schemes 1 and 2) were synthesized as previously described [40]. All other chemicals were of analytical grade and were used as received from suppliers. Anhydrous solvents were obtained according to standard distilling procedures. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz using a Bruker DRX 300 spectrometer. Mass spectra were recorded on a MALDI-TOF/TOF 4800 Applied Biosystems.

2.2. Synthesis of phthalocyanines *7–9*: general procedure

The appropriate phthalonitrile and $InCl_3 \cdot 4H_2O$ were dissolved in quinoline (0.5 mL) and the mixture was heated at 160 °C for 10–14 h under nitrogen atmosphere. After cooling, the reaction mixture was poured onto methanol (100 ml). The precipitate was filtered and washed with hot methanol. The solid was subjected to column chromatography on silica gel using a mixture of $CHCl_3$ and THF (0.5–3%) as the eluent. The main fraction was collected, evaporated and reprecipitated with methanol.



Scheme 1. Synthesis of phthalocyanine precursors [40].



Scheme 2. Synthesis of indium chloride sulfonamide substituted phthalocyanines.

2.2.1. {2,3,9,10,16,17,23,24-octakis[4-(4-methoxyphenylaminosulfonyl)phenoxy]phthalocyaninato}indium(III) chloride (*7*)

For this synthesis were used phthalonitrile **4** (200 mg, 2.93×10^{-4} mol) and $InCl_3 \cdot 4H_2O$ (28.66 mg, 9.77×10^{-5} mol). The reaction time was 14 h. Yield: 53 mg (25%). M.p. > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) (δ/ppm): 4.14 (s, 24H, CH_3), 7.31 (d, 16H, J = 8.8 Hz, H-3″), 7.59 (d, 16H, J = 8.7 Hz, H-2′), 7.52 (d, 16H, J = 8.8 Hz, H-2″), 8.16 (d, 16H, J = 8.7 Hz, H-3′), 9.46 (s, 8H, PcH). ^{13}C NMR (75 MHz, $CDCl_3$) (δ/ppm): 54.8, 113.7, 115.7, 117.1, 123.7, 128.9, 129.6, 134.6, 150.3, 156.6, 158.1, 167.3. MS (MALDI-TOF, PEG + NaI): m/z 2879.35 $[M]^{+\cdot}$, UV–Vis (DMSO) λ_{max} (log ε): 367 (4.58), 625 (4.01), 694 (4.97) nm.

2.2.2. {2,3,9,10,16,17,23,24-octakis[(4-diethylaminosulfonyl)-phenoxy]phthalocyaninato}indium(III) chloride (*8*)

For this synthesis were used phthalonitrile **5** (180 mg, 3.07×10^{-4} mol) and $InCl_3 \cdot 4H_2O$ (28.66 mg, 9.77×10^{-5} mol). The reaction time was 10 h. Yield: 44 mg (23%). M.p. > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) (δ/ppm): 1.16 (t, 48H, J = 7.1 Hz, CH_3), 3.27 (q, 32H, J = 7.1 Hz, CH_2), 7.21 (d, 16H, J = 8.7 Hz, H-2′), 7.85 (d, 16H, J = 8.7 Hz, H-3′), 9.25 (s, 8H, Pc-H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ/ppm): 14.2, 42.7, 117.0, 117.5, 129.3, 134.9, 135.4, 149.7, 152.8, 160.2. MS (MALDI-TOF, PEG + NaI): m/z 2479.9

$[M]^{+\cdot}$, 2502.9 $[M+Na]^+$, UV–Vis (DMSO) λ_{max} (log ε): 365 (4.85), 628 (4.70), 697 (5.22) nm.

2.2.3. {2,3,9,10,16,17,23,24-octakis[4-didodecylaminosulfonyl)-phenoxy]phthalocyaninato}indium(III) chloride (**9**)

For this synthesis were used phthalonitrile **6** (335 mg, 2.93×10^{-4} mol) and $InCl_3 \cdot 4H_2O$ (28.66 mg, 9.77×10^{-5} mol). The reaction time was 10 h. Yield: 170 mg (49%). ^{1}H NMR (300 MHz, $CDCl_3$) (δ/ppm): 0.87 (br, 48H, CH_3), 1.23 (br, 352H, CH_2), 3.11 (q, 32H, CH_2), 7.18–7.20 (d, 16H, H-2′), 7.82–7.88 (d, 16H, H-3′), 9.22 (s, 8H, Pc-H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ/ppm): 13.6, 22.1, 23.2, 25.6, 27.1, 29.6, 30.1, 31.4, 48.0, 115.5, 116.7, 128.9, 134.0, 135.8, 147.9, 152.5, 160.2. UV–Vis (toluene) λ_{max} (log ε): 360 (4.96), 628 (4.53), 698 (5.30) nm.

2.3. Spectroscopic measurements

Optical absorption spectra of Pcs **7–9** in DMSO and toluene were recorded with a Varian (Mod. Cary 5) UV–Vis-NIR spectrophotometer. Fluorescence and excitation spectra were obtained with a Perkin–Elmer (Mod. LS-50B) spectrometer.

2.4. Nonlinear transmission measurements

Nonlinear transmittance of Pcs **7–9** was measured at 532 nm using 9 ns pulses of a doubled Nd:YAG laser (Quantel YG980E). A pyroelectric detector (Scientech Mod. SPHD25) was used to measure the energy transmitted by the sample. 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 by a $\lambda/2$ wave-plate and a polarizing cube beam-splitter. Cuvettes with 2 mm optical path were used. The area of the illuminated spot on the sample was approximately 0.02 cm^2.

2.5. Pump and probe experiments

The transient absorption of **9** was analyzed by means of the pump and probe technique [41]. In these experiments the sample was excited with the same pulses used for the measurements of nonlinear transmission at the frequency of 10 Hz. The fluence of excitation was 0.25 J cm^{-2} per single pulse. Probing of excited-state absorption of Pc **9** was accomplished by means of the white light generated by a stabilized 150 W Xe lamp. The time-variation of nonlinear optical absorption was recorded with a 1 GHz digital oscilloscope (LeCroy LC564A). One hundred signals were averaged in order to keep a high signal-to-noise ratio. A Jobin–Yvon Horiba TRIAX 320 spectrometer, equipped with 600 and 300 groove mm^{-1} gratings, and a phototube Hamamatsu R2257 with rise time 2.6 ns, have been used to record the probe signal.

3. Results and discussion

3.1. Synthesis

Sulfonamide-substituted phthalonitriles **4**–**6**, immediate precursors of phthalocyanines **7–9**, were synthesized starting from the commercially available 4,5-dichlorophthalonitrile (**1**) (Scheme 1) [40]. Reaction of **1** with phenol, in the presence of potassium carbonate, afforded 4,5-diphenoxyphthalonitrile (**2**). Treatment of 4,5-diphenoxyphthalonitrile with chlorosulfonic acid produced the 4,5-bis(4-chlorosulfonyphenoxy)phthalonitrile **3**. Reaction of **3** with different amines, namely *p*-anisidine, diethylamine and didodecylamine, gave the desired sulfonamide derivatives **4**, **5** and **6**, respectively.

Simple cyclotetramerization of precursors **4**–**6** in quinoline at 160 °C, in the presence of $InCl_3$, gave the desired indium chloride phthalocyanine complexes **7**–**9**, respectively (Scheme 2). All characterization data are in agreement with the proposed structures (see Section 2).

3.2. UV–Vis spectra

Absorption spectra of complexes **7–9** were determined in different solvents (**7** and **8** in DMSO, and **9** in toluene) in order to minimize possible effects of aggregation during the successive evaluation of their nonlinear transmission properties (*vide infra*). All the electronic absorption spectra display the typical spectral features of Pcs; the characteristic B- and Q-bands [42] appear respectively at 356 and 690 nm (**7**), 362 and 689 nm (**8**), and 368 and 697 nm (**9**). The group of absorption bands in the range 600–675 nm are originated from vibronic transitions that are associated with the main Q-band transition [42].

It is evident from Fig. 1 that the nature of the SO_2N-substituent in Pcs **7**–**9** does not affect the position of the main absorption peaks. This indicates that transition energies of **7**–**9** involve mainly frontier orbitals that are localized on the phthalocyanine ring. Therefore, the chosen N-substituents do not alter the extent of electronic conjugation in **7**–**9** with respect to an unsubstituted phthalocyanine. This holds also true in the case of **7**, which bears aryl substituents. These spectra indicate that the new phthalocyanines retain their electronic features irrespectively of the nature of the sulfonamide substituents. This fact can be advantageously used to obtain new phthalocyanine derivatives with different solubility profiles just by changing the amine used in step of the sulfonamide formation (Scheme 1).

3.3. Emission and excitation spectra

The emission and excitation spectra of phthalocyanines **7**, **8** and **9** are shown in Figs. 2–4 together with the respective normalized absorption spectra.

The emission spectra of **7**, **8** and **9** display small Stokes shift with respect to the Q-band position with the main emission band located at about 700 nm [43]. Structures of vibronic emissions mirror those located at longer wavelengths with respect to the main emission peak. The lack of any dependence on the presence of oxygen in solution and the observation of small Stokes shift indicate that the measured emission is due to fluorescence and not phosphorescence [44]. The excitation spectra of Pcs **7**–**9** were determined recording the emission at 700 nm, i.e. the wavelength of

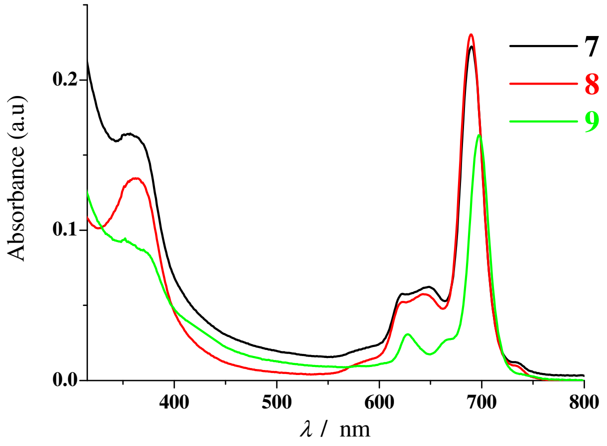


Fig. 1. Absorption spectra of **7** (black trace) and **8** (red trace) in DMSO and **9** (green trace) in toluene. For the evaluation of the molar extinction coefficients see analytical data in the Section 2.

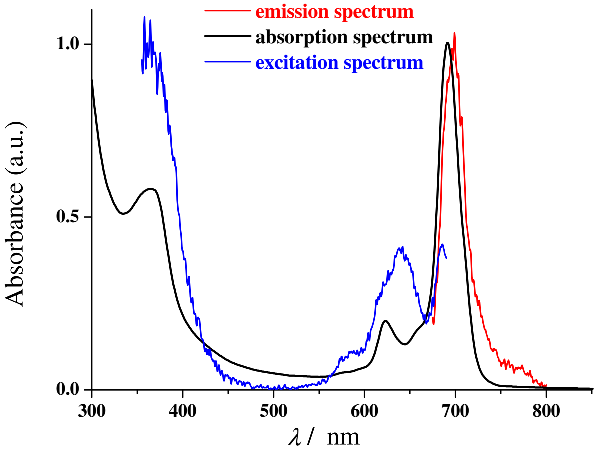


Fig. 2. Normalized absorption (black trace), emission (red trace) and excitation spectra for **7** in DMSO. For the determination of the emission spectrum the excitation wavelength was 622.5 nm. Emission wavelength was 698 nm for the analysis of excitation spectrum.

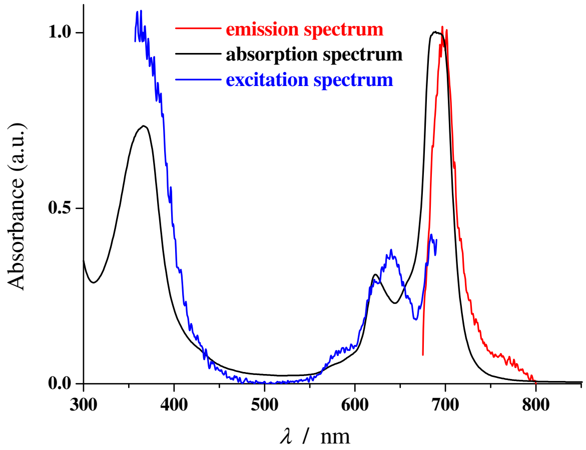


Fig. 3. Normalized absorption (black trace), emission (red trace) and excitation spectra for **8** in DMSO. For the determination of the emission spectrum the excitation wavelength was 622.5 nm. Emission wavelength was 699 nm for the analysis of excitation spectrum.

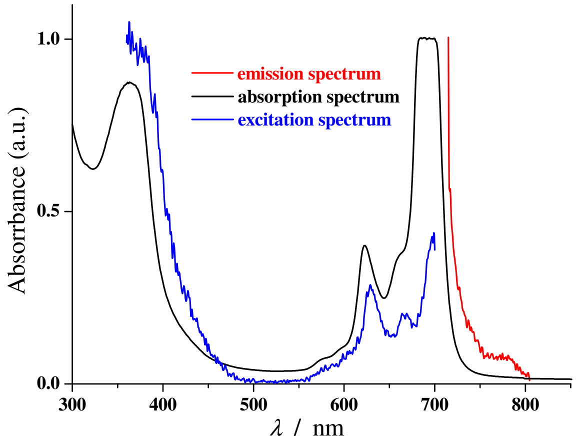


Fig. 4. Normalized absorption (black trace), emission (red trace) and excitation spectra for **9** in toluene. For the determination of the emission spectrum the excitation wavelength was 622.5 nm. Emission wavelength was 715 nm for the analysis of excitation spectrum.

their maximum emission (Figs. 2–4). As expected, due to the rigidity of the macrocycle, a very small Stokes shift is observed [44].

3.4. Nonlinear transmission

Fig. 3 shows the variations of transmittance of DMSO solutions of **7** and **8**, and of a toluene solution of **9** with the incident fluence at 532 nm.

The decrease of optical transmission with increasing incident fluence indicates that **7**, **8** and **9** are reverse saturable absorbers [14–19]. Pc **9** displays the better limiting properties reaching a minimum of 13% of the linear transmission at about 1 J cm^{-2} of incident fluence (Fig. 5). The limiting threshold, F_{lim}, i.e. the fluence at which the transmittance is half the value of linear transmittance [45], is 0.39 and 0.13 J cm^{-2} for **8** and **9**, respectively (Fig. 5). In the case of **9**, F_{lim} is comparable to that of other indium phthalo- and naphthalocyanines with axial halogens [26–38]. In the case of complex **7**, the limiting threshold could not be exactly determined within the experimental range of incident fluences. From the profile of nonlinear transmission it is evaluated F_{lim} (**7**) >1 J cm^{-2}. The observed larger limiting thresholds of **7** and **8**, with respect to **9**, indicate that the presence of long-chain substituents in **9** is beneficial for the improvement of the nonlinear transmission properties within this series of sulfonamide substituted phthalocyanines. This suggests that the nonlinear optical properties of sulfonated compounds **7**–**9** are mainly dependent on their capability to prevent intermolecular aggregation [46–50]. The occurrence of RSA by Pcs **7**–**9** has three main implications about the nature and the characteristics of their involved excited states: (a) the excited state has a larger absorption cross-section with respect to the ground state S_0 at the wavelength of excitation; (b) their lifetimes τ_{exc} fulfil the condition $\tau_{\text{exc}} \geqslant \tau_{\text{p}}$, where τ_{p} represents the laser pulse width, and (c) the formation time of their excited states is much shorter than the duration of the laser pulse. Since ns pulses are used, the above considerations confirm that, similar to other indium phthalocyanine- and naphthalocyanine-based systems [26–38]. RSA of Pcs **7**–**9** is produced by one-photon absorption from the optically pumped excited triplet state T_1 in a process of sequential multiphoton absorption [51–55].

Among Pcs **7**–**9** only **9** displays the flattening of the nonlinear transmission curve when $F_{\text{in}} > 0.8$ J cm^{-2} (Fig. 5). This feature allows to calculate a relevant parameter [18] for the evaluation of the optical power limiting properties of **9**. In fact, in correspon-

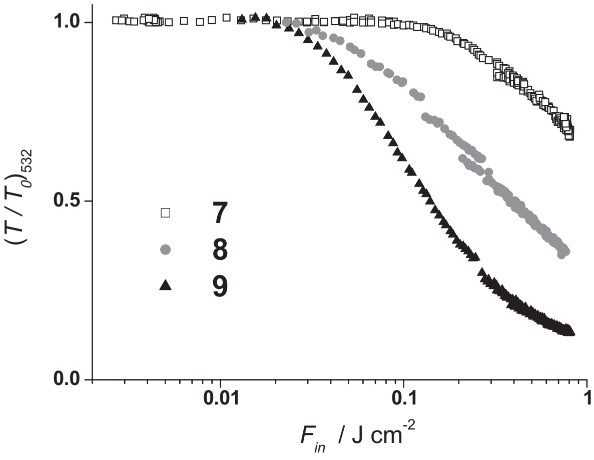


Fig. 5. Variation of the normalized transmission of Pcs **7**–**9** at 532 nm (cuvette thickness: 2 mm). Sample was excited with 9 ns pulses. Linear transmittance was 0.75 for all three solutions. Solutions concentrations were: 2.7 × 10^{-4} M for **7** in DMSO; 3.6 × 10^{-4} M for **8** in DMSO; 2.0 × 10^{-4} M for **9** in toluene.

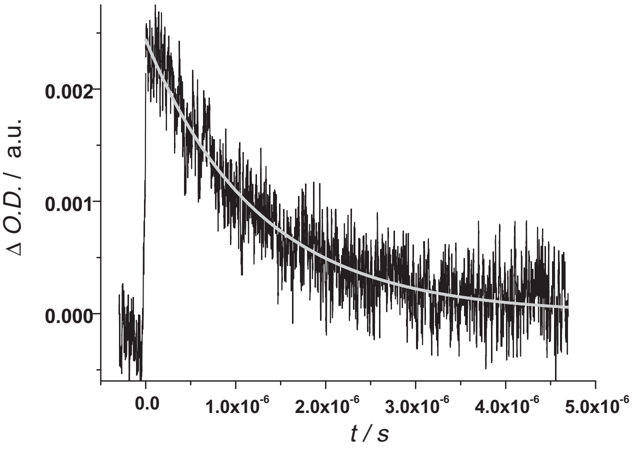


Fig. 6. Temporal variation of the differential absorbance, ΔO.D., at 485 nm for **9** in toluene upon excitation at 532 nm with ns pulses (C_1: 2×10^{-4} M; F_{in}: 0.25 J cm^{-2}). Profile is obtained as an average of 150 consecutive traces with $t = 0$ s corresponding to the time at which laser pulse starts. Mono-exponential fit (grey line) is also shown when time constant is 1.25 μs.

dence of such a minimum of transmittance, it can be assumed that Pc **9** is fully promoted into the excited triplet T_1 state (Fig. 4) with an effective one-photon absorption cross-section σ' given by Eq. (1):

$$\sigma'\lambda = \ln[1/T_{\min}\lambda]/Nl \quad (1)$$

In Eq. (1), N is the concentration of **9** in molecules cm^{-3}, and l indicates the solution thickness in cm. $T_{\min}$ represents the minimum transmittance that is achieved by the nonlinear absorber. It corresponds to the transmittance value at the end of the sigmoid curve of nonlinear transmission (Fig. 5). From the experimental data of Fig. 5 one finds $\sigma' = 9.6 \times 10^{-17}$ cm^2 at 532 nm, being $T_{\min} = 0.1$, $N = 1.2 \times 10^{17}$ mol/cm^{-3} and $l = 0.2$ cm. The value of the figure of merit $\kappa = \sigma'/\sigma_0$ [26] at 532 nm is 8 for Pc **9**, as the value of the ground state absorption cross section, σ_0, is 1.2×10^{-17} cm^2 (11 940 M^{-1} cm^{-1}), at the same wavelength. The comparison with other indium complexes displaying $\kappa \leqslant 5$ [29,30,35,36,44], reveals that octasulfonated indium complex **9** is an efficient multiphoton absorber for optical power limiting purposes within this class of molecular materials.

*3.5. Transient absorption of **9***

The excited state responsible for the nonlinear absorption properties of **9** has been characterized by means of pump and probe measurements using degassed toluene solutions of Pc **9** [33,41]. Time-variation of the differential absorbance (ΔO.D.) at 485 nm has been recorded during the first 5 μs following laser pulse at $t = 0$ (Fig. 6).

The experiment of pump and probe in Fig. 6 has been conducted when $F_{in} = 0.25$ J cm^{-2} using the same laser pulses of the nonlinear transmission experiment (Fig. 5). Transient signal produced by the nonlinear absorption of **9** at 485 nm could be fitted with a mono-exponential decay having a time constant of 1.25 μs (Fig. 6). Such a value corresponds to the lifetime of the triplet excited state of **9** that produces the effect of reverse saturable absorption of ns visible light pulses.

4. Conclusions

Indium(III) octasulfonamidophthalocyanines **7**, **8** and **9** were prepared and their nonlinear optical properties were evaluated. In solution, all three compounds behave as reverse saturable absorbers of ns pulses with limiting thresholds of >1, 0.39 and 0.13 J cm^{-2} for **7**, **8** and **9**, respectively. Such a trend indicates that nonlinear optical properties of complexes **7**–**9** are mainly controlled by their tendency of forming molecular aggregates during the process of nonlinear absorption. In fact, the phthalocyanine **7**, due to the presence of acidic SO_2NHAr protons has a higher aggregation propensity than the analogous SO_2NR_2 substituted phthalocyanines **8** and **9**. Comparing phthalocyanines **8** and **9**, it is confirmed that the larger the substituents the better the optical limiting performance. Only complex **9** display a complete sigmoid-shaped profile of nonlinear transmission at 532 nm. This feature allowed the determination of the absorption cross-section of the excited state of **9** that produced the effect of reverse saturable absorption at that wavelength. The excited-state absorption cross-section of **9** was calculated as 9.6×10^{-17} cm^2, which corresponds to a merit factor of 8. The transient absorption experiment showed that the excited state responsible for the effect of reverse saturable absorption of **9** has a triplet manifold with lifetime of 1.25×10^{-6} s.

Acknowledgments

Thanks are due to Fundação para a Ciência e a Tecnologia (FCT), (COMPETE – Programa Operacional Factores de Competitividade), QREN/FEDER for funding the Organic Chemistry Research Unit and the Projects PPTDC/DG/QUI/82011/2006 and PTDC/QUI/74150/2006. M.J.F. Calvete also thanks FCT for his post-doc grant (SFRH/BPD/26775/2006).

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