J. Phys. Chem. A **2008,** *112,* 8515–8522

Indium Phthalocyanines with Different Axial Ligands: A Study of the Influence of the Structure on the Photophysics and Optical Limiting Properties

Danilo Dini,*,† Mario J. F. Calvete,‡ Michael Hanack,‡ and Moreno Meneghetti†

Institute of Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany, and Department of Chemical Sciences, University of Padua, Via Marzolo 1, I-35131 Padua, Italy

Received: April 05, 2008; Revised Manuscript Received: June 03, 2008

The photophysical properties of four axially substituted indium phthalocyanines, namely, 2,(3)-tetra-*tert*-butyl-phthalocyaninato indium chloride (**1**), 2,(3)-tetra-[(3,5-di-*tert*-butyl)-phenyloxy]-phthalocyaninato indium bromide (**2**), 2,(3)-tetra-[(3,5-di-*tert*-butyl)-phenyloxy]-phthalocyaninato indium iodide (**3**), and 2,3-octa-[(2-hexyl)-ethyloxy]-phthalocyaninato indium trifluoroacetate (**4**), have been investigated, and their optical limiting properties with nanosecond light pulses were evaluated. All complexes behave as reverse saturable absorbers in the range of 400−625 nm due to a triplet−triplet excited-state transition. Excited-state absorption cross sections and triplet state lifetimes are not significantly affected by the nature of the axial ligand. On the other hand, remarkable differences in the variation of nonlinear transmittance are observed for **1**−**4** due to significantly different intersystem crossing rates. Heavier axial ligands in phthalocyanines **2** and **3** produce the largest variations of nonlinear transmission (heavy-atom effect). Complex **1** in polystyrene matrix shows reversible nonlinear absorption when incident fluence does not exceed 0.025 J cm^{-2}.

Introduction

Phthalocyanines (Pcs) are highly symmetrical complexes with D_{4h} symmetry, which possess an extended network of 44 conjugated π-electrons. This combination of features imparts strong optical absorption in the visible spectrum with molar extinction coefficient (ε) values as large as 10^5 M^{-1} cm^{-1} in correspondence of the characteristic Q-band.[1] Beside that, Pcs can also achieve fast, large, and reversible optical nonlinearities like reverse saturable absorption (RSA).[2,3] 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.[4] In doing so Pcs and analogues have found a prominent place as active materials for the important application of optical power limiting (OPL) in the passive self-activated mode.[2a,5] The reason for the large employment of Pcs is related to the possibility of varying the Pc structure and, consequently, its electronic configuration in a controlled fashion through peripheral substitution, variation of the central atom, and modification of the axial ligand.[6] In some cases the design and realization of Pcs has successfully led to the optimization of their nonlinear optical properties with respect to reference materials as far as OPL of nanosecond pulses in the visible range was concerned.[3a,b,e,7] In particular, indium(III) phthalocyanines[3b,e,4b,7b,e,8] and naphthalocyanines[7a,c,f,i,9] showed relatively higher efficiency as OPL materials in the wide spectral range of $390 < \lambda < 1100$ nm in comparison to analogous metal complexes.[3b,4b,7d,9d,10] The optimization of the nonlinear optical properties of such Pc complexes for the limiting of nanosecond pulses in the visible spectrum was achieved through the recognition of a mechanism of sequential multiphoton absorption,[11] which involves highly absorbing excited triplet states with short time of formation (in the order of 10^{-12}−10^{-11} s)[9f] and long lifetime (>200 ns)[4i,9f,11b] in comparison to the duration of the laser pulse (≈10 ns). The highly absorbing excited triplet state T_1 is generated via a step of intersystem crossing (ISC), i.e., upon decay of the first excited singlet state S_1 which has been populated through the absorption of the first photon from the ground-state S_0 (Figure 1).[4i,9f,11b] The isc step is particularly accelerated in indium and lead complexes due to the heavy-atom effect generated by these central metals.[3b,7f,i,11] Moreover, quantum yield of triplet formation results increased by the presence of these metals in the sequential multiphoton absorption process of their phthalo- and naphthalocyaninates.[7i,10a] The first excited triplet state of these complexes is not directly populated by the alternative one-photon transition $S_0 \rightarrow T_1$,[4i,9f,11b] and second photon absorption takes place via the excited triplet states transition $T_1 \rightarrow T_2$ (Figure 1).[4i,7f,8a,f,9a,b,f,11b] This sequence of events implies the involvement of four levels[2d] in the model that accounts for the nonlinear optical behavior of indium phthalo- and naphthalocyanines upon excitation with nanosecond laser pulses.

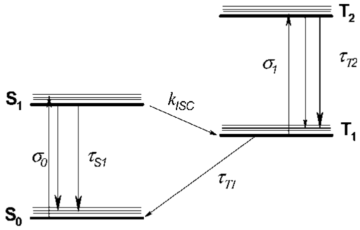

Figure 1. Jablonski diagram describing the mechanism of sequential multiphoton absorption of intense pulsed light by indium phthalocyanines in the visible spectrum. S_0, S_1, and $T_{1(2)}$ indicate the ground state, first excited singlet state, and first (second) excited triplet state, respectively. σ_0, σ_1, τ_{S1}, τ_{T1}, and τ_{T2} are the ground-state absorption cross section, excited triplet absorption cross section, lifetime of the first excited singlet state, lifetime of the first excited triplet state, and lifetime of the second excited triplet state, respectively. k_{ISC} represents the intersystem crossing rate.

Additionally, it has been demonstrated that OPL from PcInXs can be further increased through appropriate variations of the

---

* Corresponding author.
† University of Tübingen.
‡ University of Padua.

10.1021/jp802960s CCC: $40.75

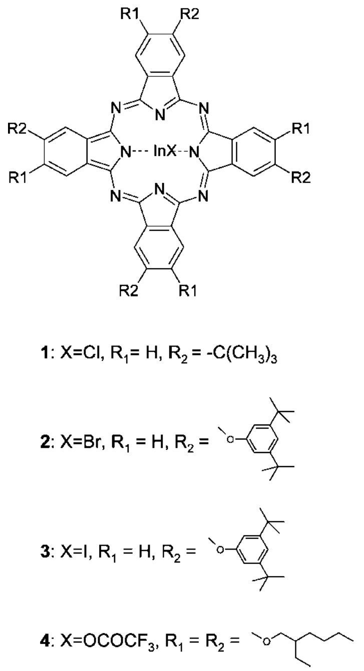

Figure 2. Differently substituted indium phthalocyanines **1**−**4** for nonlinear optical transmission (NLO) studies with nanosecond laser pulses.

axial ligand X which is coordinated by central indium.[3e,7e,i] In fact, favorable effects on the OPL of PcInXs are produced by axial ligands with high atomic number,[7e,i] high electronic polarizability,[7a,d] large sterical hindrance,[7d,e,i] and large dipole moments having perpendicular orientation with respect to the plane of the Pc ring.[3e,12] Such structural modifications bring about the reduction of intermolecular interactions and the consequent quenching of excitation, the increase of the transition dipole moment in the processes of excited-state absorption, additional heavy-atom effect, and increase of higher order hyperpolarizabilities.[4g] Since axial substitution in PcInXs constitutes one of the most effective approaches for the improvement of OPL properties in these complexes, we tackled the preparation of four different axially substituted PcInXs, namely 2,(3)-tetra-*tert*-butyl-phthalocyaninato indium chloride (*t*-Bu_4PcInCl, **1**),[3b,e] 2,(3)-tetra-[(3,5-di-*tert*-butyl)-phenyloxy]-phthalocyaninato indium bromide [(*t*-Bu_2PhO)$_4$PcInBr, **2**], 2,(3)-tetra-[(3,5-di-*tert*-butyl)-phenyloxy]-phthalocyaninato indium iodide [(*t*-Bu_2PhO)$_4$PcInI, **3**], and 2,3-octa-[(2-hexyl)-ethyloxy]-phthalocyaninato indium trifluoroacetate (EHO$_8$PcInTFA, **4**)[3f] (Figure 2) taking advantage of the easiness of preparation for this type of indium complexes. Similar to our precedent study on axially halogenated indium naphthalocyanines,[7i] the series of phthalocyanines **1**−**4** has been prepared with the aim of analyzing the influence of the axial ligand on nonlinear transmission properties at 532 nm, excited-state spectra, and dynamics in solution. Moreover, the nonlinear transmission properties of the indium phthalocyanine **1** have been also determined when included in polystyrene thin solid film.[9d]

Experimental Section

Synthesis. The preparation of *t*-Bu_4PcInCl (**1**) has been accomplished following the synthetic procedures reported in refs 3 and 13. Dispersion of indium phthalocyanine **1** in polystyrene film has been realized according to the method described in ref 9d.

***(t-Bu$_2$PhO)$_4$PcInBr*, 2.** The precursor 4-[(3,5-di-*tert*-butyl)-phenoxy]-phthalonitrile (**5**) was prepared upon condensation of 4-nitro-phthalonitrile[14] with 3,5-di-*tert*-butyl-phenol[15] in mild basic conditions.[16] Dinitrile **5** (1.66 g, 5 mmol) and $InBr_3$ (580.0 mg, 1.65 mmol) were mixed in 1-chloronaphthalene (1.5 mL) and heated to 180 °C for 2.5 h. After cooling the reaction mixture was poured into methanol (100 mL) and stirred. The precipitate was collected and washed with hot methanol to give **2** as a dark yellow-green solid (0.76 g, yield: 40%). ^{13}C NMR (250 MHz; THF-d_8; Me$_4$-Si): $\delta = 31.3$, 34.9, 112.6, 113.8, 117.3, 134.3, 150.4, 152.4, 154.4, 155.2, 156.9 ppm. ^{1}H NMR (250 MHz; THF-d_8; Me$_4$-Si): $\delta = 1.25$ (s, 72 H), 7.05 (s, 8 H), 7.17 (s, 4 H), 7.64 (d, 4 H), 8.95 (s broad, 8 H) ppm. MS (FD): *m*/*z* 1513.1 [M$^+$] (molecular peak: 1512.41 Da). Elemental analysis: found 71.5% C (theoretical 69.89% C); found 7.7% N (theoretical 7.41% N); found 5.9% H (theoretical 5.60% H).

***(t-Bu$_2$PhO)$_4$PcInI*, 3.** Dinitrile **5**[14−16] (1.66 g, 5 mmol) and InI_3 (820.0 mg, 1.65 mmol) were mixed in 1-chloronaphthalene (1.5 mL) and heated to 180 °C for 2.5 h. After cooling the reaction mixture was poured into methanol (100 mL) and stirred. The precipitate was collected and washed with hot methanol to give **3** as a dark yellow-green solid (0.82 g, yield: 42%). ^{13}C NMR (250 MHz; THF-d_8; Me$_4$-Si): $\delta = 31.3$, 34.9, 112.9, 113.7, 117.3, 134.4, 150.4, 152.4, 154.6, 155.3, 156.8 ppm. ^{1}H NMR (250 MHz; THF-d_8; Me$_4$-Si): $\delta = 1.25$ (s, 72 H), 7.08 (s, 8 H), 7.19 (s, 4 H), 7.66 (d, 4 H), 8.99 (s broad, 8 H) ppm. MS (FD): *m*/*z* 1560.2 [M$^+$] (molecular peak: 1559.41 Da). Elemental analysis: found 68.5% C (theoretical 67.78% C); found 7.5% N (theoretical 7.19% N); found 5.7% H (theoretical 5.43% H).

***EHO$_8$PcInTFA*, 4.** The synthesis of the phthalocyaninato indium triflouroacetate **4** has been previously reported in ref 3f.

Photophysical Measurements. Optical spectra were recorded with a Varian Cary 5 UV−vis−NIR spectrophotometer in 2 mm thick cells. Fluorescence spectra of phthalocyanine solutions were obtained with a Perkin-Elmer LS 50B spectrometer using 10 mm Suprasil quartz cells.

Nonlinear Optical Transmission Measurements. Nonlinear optical transmission measurements were carried out with 9 ns pulses at 532 nm from a doubled Nd:YAG laser (Quantel YG980E). Transmitted energies were measured with a pyroelectric detector (Scientech model SPHD25) by averaging 10 measurements at 1 Hz in the open-aperture configuration. Intensity of the incident pulses was controlled with a $\lambda/2$ wave plate and a polarizing cube beam splitter. The illuminated spot on the sample had an area of about 6 mm^2 in order to minimize the influence of border effects which can be present, for example, using smaller areas as in *Z*-scan measurements. The length of the optical path within the sample was 2 mm.

Pump and Probe Experiments. Pump and probe measurements were obtained with the same pulses used for the optical limiting measurements. In these experiments the sample was excited at 532 nm with 9 ns pulses at the frequency of 5 Hz. The excitation fluence was in the range of 0.2−0.4 J cm^{-2} per single pulse. Probing of nonlinear absorption of phthalocyanines **1**−**4** was accomplished by means of the white light generated by a stabilized 250 W tungsten lamp. A Jobin-Yvon Horiba TRIAX 320 spectrometer, equipped with 600 and 300 groove mm^{-1} gratings, and a Hamamatsu R2257 phototube with rise time 2.6 ns, have been used to record the probe signal. The time variations of phototube response have been recorded at every wavelength with a 1 GHz digital oscilloscope (LeCroy LC564A). Averaging of 100 signals was used for obtaining a better signal-to-noise ratio.

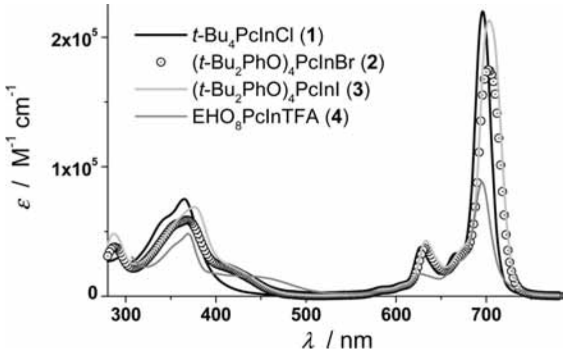

Figure 3. Molar extinction coefficient, ε, for toluene solutions of t-$Bu_4PcInCl$ (**1**), (t-$Bu_2PhO)_4PcInBr$ (**2**), (t-$Bu_2PhO)_4PcInI$ (**3**), and $EHO_8PcInTFA$ (**4**).

Results and Discussion

UV−Vis Absorption. The UV−vis absorption spectra of indium phthalocyanines **1**−**4** are presented in Figure 3.

Absorption spectra are characteristic of Pcs[1a,b] in solution with the Q-bands centered at 696, 702, 702, and 695 nm for **1**, **2**, **3**, and **4**, respectively. The small differences between these values can be mostly related to the variation of the extent of electronic conjugation from the peripheral substituents of the Pc ring[7b] rather than a direct consequence of the variation of axial ligand in Pcs **1**−**4** (Figure 2).[7i] Shoulders of the Q-bands are recognized to be of vibronic nature.[1] B-bands are located at 365, 368, 376, and 369 nm for **1**, **2**, **3**, and **4**, respectively. Also in this case one finds a scarce influence of the axial ligand nature on the location of B-bands for Pcs **1**−**4**. Pcs concentrations of the solutions used to record the UV−vis spectra of **1**−**4** (Figure 3) ranged in the interval 10^{-5}−10^{-4} M. At these concentrations no spectral evidence of molecular aggregation[17] in solution was found.

Emission. Emission and excitation spectra of indium phthalocyanines **1**−**4** in toluene are shown together with their absorption profiles in Figure 4. Maxima of emission spectra have been normalized with respect to the height of the Q-band absorption.

Emission profiles of PcInXs **1**−**4** (open circles in Figure 4) have been obtained upon excitation at the wavelengths of B-band absorption (Figure 3), which corresponds to the transition HOMO(−1)−LUMO.[1] Emission curves have a typical mirror image with respect to the absorption curves and generally display a Stoke shift of the main emission band.[18] Emission maxima are located at 718, 722, 723, and 702 nm for PcInXs **1**, **2**, **3**, and **4**, respectively. One observes larger Stoke shifts for the halogenated systems **1**−**3**[19] with respect to $EHO_8PcInTFA$ (**4**) (Figure 4). The small shifts and the lack of dependence of the emissions from the presence of oxygen show that they originate from fluorescence.

Excitation spectra (gray lines in Figure 4) were recorded at the wavelengths of Pcs maximum emission. In these profiles two main groups of excitation can be recognized: one deriving from the B-band, the second from the Q-band with its vibronic structure, as usually found for this class of compounds.[6b,18] In case of halogenated PcInXs **1**−**3** one recognizes two broad peaks centered at about 635 and 660 nm (Figure 4a−c). The relative heights of these two excitation peaks change within the halogenated series, in particular, when passing from **1** to **2**, whereas **2** and **3** present very similar profiles. Different from halogenated systems **1**−**3**, the excitation spectrum of $EHO_8PcInTFA$ (**4**) is dominated by the sole peak at about 630 nm (Figure 4d). In fact, B-band excitation produces relatively little emission in comparison to 630 nm excitation in **4**.

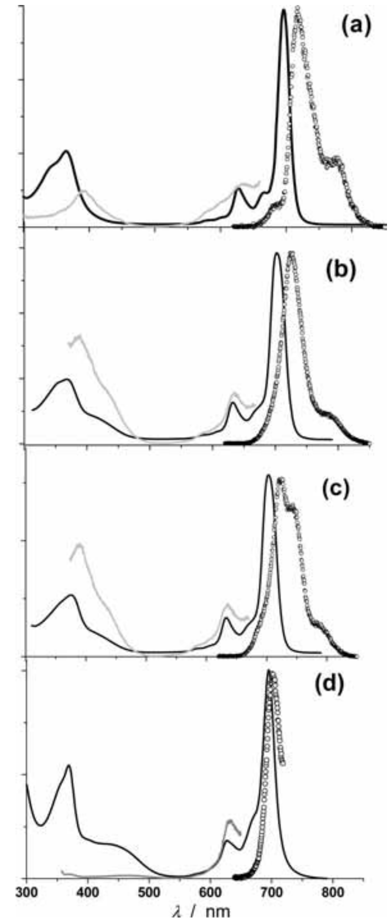

Figure 4. Absorption (black trace), emission (open circles), and excitation (gray trace) spectra of (a) t-$Bu_4PcInCl$ (**1**), (b) (t-$Bu_2PhO)_4PcInBr$ (**2**), (c) (t-$Bu_2PhO)_4PcInI$ (**3**), and (d) $EHO_8PcInTFA$ (**4**) in toluene. Emission spectra have been generated upon excitation at (a) 364, (b) 368, (c) 375, and (d) 370 nm. Excitation spectra of Pcs **1**−**4** have been determined recording the emission at (a) 718, (b) 722, (c) 723, and (d) 702 nm.

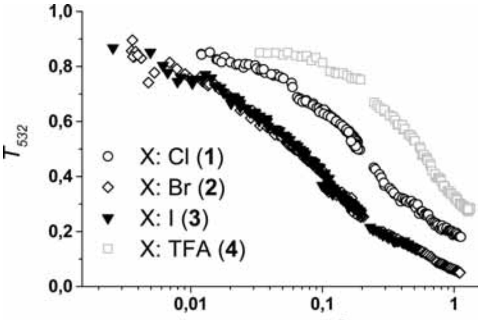

Figure 5. Nonlinear transmittance at 532 nm, T_{532}, for PcInXs **1**−**4** in toluene. t-$Bu_4PcInCl$ (**1**), (t-$Bu_2PhO)_4PcInBr$ (**2**), (t-$Bu_2PhO)_4PcInI$ (**3**), and $EHO_8PcInTFA$ (**4**) were excited at 532 nm with nanosecond pulses. Cuvette thickness: 2 mm.

Nonlinear Optical Transmission. Indium phthalocyanines **1**−**4** behave as reverse saturable absorbers[2] to nanosecond pulses at 532 nm since a reversible decrease of optical transmission, T_{532}, is observed upon increase of the incident fluence, F_{in} (Figure 5).

TABLE 1: Values of Limiting Threshold at 532 nm [F_{lim}(532)] for the Toluene Solutions of PcInXs 1−4

compound	F_{lim}(532)/J cm^{-2}
t-Bu$_4$PcInCl (**1**)	0.25
(t-Bu$_2$PhO)$_4$PcInBr (**2**)	0.09
(t-Bu$_2$PhO)$_4$PcInI (**3**)	0.09
EHO$_8$PcInTFA (**4**)	0.66

TABLE 2: Lifetimes of the First Excited Triplet State, τ_{T1}, of Pcs 1−4 as Determined through a Monoexponential Fit of the Profiles in Figure 6

compound	τ_{T1}/μs
t-Bu$_4$PcInCl (**1**)	0.57
(t-Bu$_2$PhO)$_4$PcInBr (**2**)	0.72
(t-Bu$_2$PhO)$_4$PcInI (**3**)	0.69
EHO$_8$PcInTFA (**4**)	0.84

From the nonlinear transmission profiles of Figure 5 we extrapolated the values of limiting threshold (Table 1), F_{lim}, i.e., the fluence at which the transmittance becomes half the linear one, T_0 ($T_0 = 0.84$ for all the solutions).[20]

Comparison of F_{lim} values indicates that complexes with axial bromide and iodide have the lowest values (<0.1 J cm^{-2}), whereas EHO$_8$PcInTFA (**4**) presents the highest one (>0.6 J cm^{-2}). In terms of OPL performance, the lower the value of F_{lim}, the higher the limiting effectiveness of the material.[2a] Therefore, complexes **2** and **3** result in the most useful examples for OPL applications.

Occurrence of RSA to nanosecond pulses at 532 nm via a mechanism of excited-state absorption (Figure 1) has several implications about the excited states of PcInXs **1−4** which generate it. First, excited triplet states T$_1$ of PcInXs **1−4** must possess larger absorption cross sections, σ_1 (Figure 1), with respect to the ground state at the wavelength of irradiation. Second, RSA of pulsed radiations indicates that lifetimes of T$_1$ states for indium phthalocyanines **1−4** are of the same order of magnitude or larger than the pulse width (laser pulses have fwhm = 9 ns).[10a,b] Another consequence of RSA by PcInXs **1−4** concerns the rising times of T$_1$ excited states. These are bound to excitation width since the time necessary to form excited triplet states T$_1$ via intersystem crossing (Figure 1) has to be shorter than light pulse duration.[3e,8a,21]

Triplet Excited-State Characterization. Time-resolved variations of differential absorbance between triplet excited state and ground state, ΔOD, have been recorded at different wavelengths for PcInXs **1−4** in deaerated toluene solutions (Figure 6).

From the temporal variations of differential absorbance the lifetimes τ_{T1} of the excited triplet states T$_1$ were determined for indium phthalocyanines **1−4** (see Table 2).

Computed values of τ_{T1} are in the order of fractions of microseconds and do not show a strong dependence on axial ligand. The transient spectra associated to the transition T$_1$ → T$_2$ (see Figure 1) are shown in Figure 7 at different times from the laser pulse. The spectra are characteristic of the triplet excited states of Pcs[3e,8f] and show that PcInXs triplet states, in the spectral range of 400−625 nm, have larger absorption cross section than the ground states. This is the spectral range where the ground states of **1−4** show an absorption minimum.

Determination of Kinetic Parameters of the Multiphoton Absorption Process. It is well-known that RSA of nanosecond pulses by PcInXs solutions is based on sequential two-photon absorption[2,22] which involves a T$_1$ → T$_2$ transition[3,10] (Figure 1).[8f] Such a model allows the fitting of nonlinear transmission data (Figure 5) by the following set of differential equations which describe the dynamics of ground-state and excited-state populations during the process of multiphoton absorption (Figure 1):[8f]

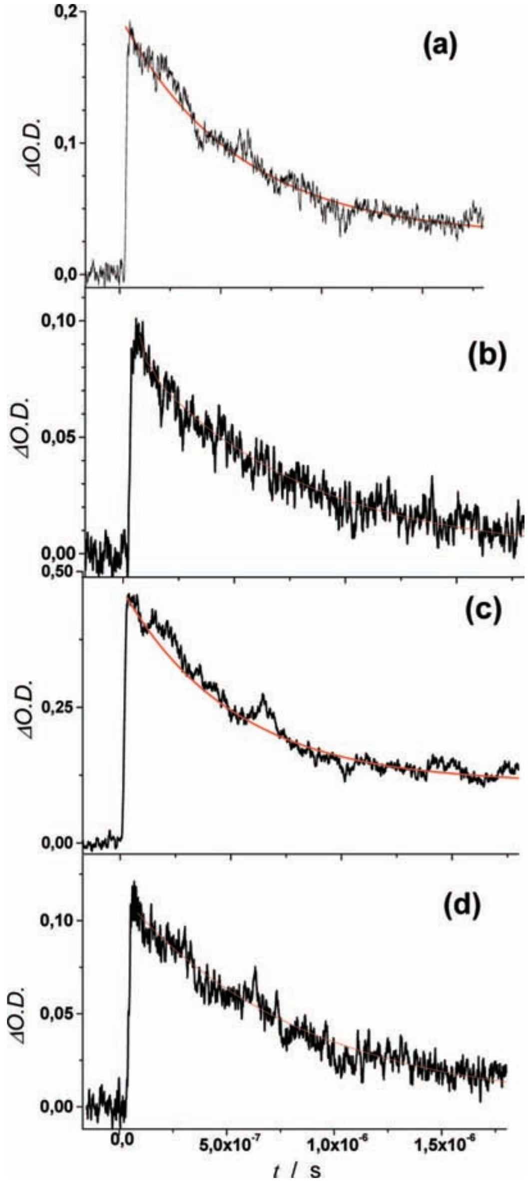

Figure 6. Temporal variations of differential absorbance, ΔOD, at 515 nm for (a) t-Bu$_4$PcInCl (**1**), (b) (t-Bu$_2$PhO)$_4$PcInBr (**2**), (d) EHO$_8$PcInTFA (**4**), and 500 nm for (c) (t-Bu$_2$PhO)$_4$PcInI (**3**). PcInXs **1−4** were dissolved in toluene and excited at 532 nm with nanosecond pulses being F_{in} = (a) 0.37, (b) 0.28, (c) 1.31, and (d) 0.37 J cm^{-2}. Monoexponential fits are indicated with the red line.

$$\frac{\mathrm{d}N_{\mathrm{S0}}}{\mathrm{d}t} = -\sigma_0 N_{\mathrm{S0}} \mathcal{I}_{\mathrm{in}} + \sigma_0 N_{\mathrm{S1}} \mathcal{I}_{\mathrm{in}} + \frac{N_{\mathrm{S1}}}{\tau_{\mathrm{S1}}} + \frac{N_{\mathrm{T1}}}{\tau_{\mathrm{T1}}} \tag{1a}$$

$$\frac{\mathrm{d}N_{\mathrm{S1}}}{\mathrm{d}t} = \sigma_0 N_{\mathrm{S0}} \mathcal{I}_{\mathrm{in}} - \sigma_0 N_{\mathrm{S1}} \mathcal{I}_{\mathrm{in}} - \frac{N_{\mathrm{S1}}}{\tau_{\mathrm{S1}}} - k_{\mathrm{isc}} N_{\mathrm{S1}} \tag{1b}$$

$$\frac{\mathrm{d}N_{\mathrm{T1}}}{\mathrm{d}t} = k_{\mathrm{isc}} N_{\mathrm{S1}} - \sigma_1 N_{\mathrm{T1}} \mathcal{I}_{\mathrm{in}} + \sigma_1 N_{\mathrm{T2}} \mathcal{I}_{\mathrm{in}} - \frac{N_{\mathrm{T1}}}{\tau_{\mathrm{T1}}} + \frac{N_{\mathrm{T2}}}{\tau_{\mathrm{T2}}} \tag{1c}$$

$$\frac{\mathrm{d}N_{\mathrm{T2}}}{\mathrm{d}t} = \sigma_1 N_{\mathrm{T1}} \mathcal{I}_{\mathrm{in}} - \sigma_1 N_{\mathrm{T2}} \mathcal{I}_{\mathrm{in}} - \frac{N_{\mathrm{T2}}}{\tau_{\mathrm{T2}}} \tag{1d}$$

In eqs1a−1d N_{S0}, N_{S1}, N_{T1}, and N_{T2} represent the population densities of the (singlet) ground state, first excited singlet state,

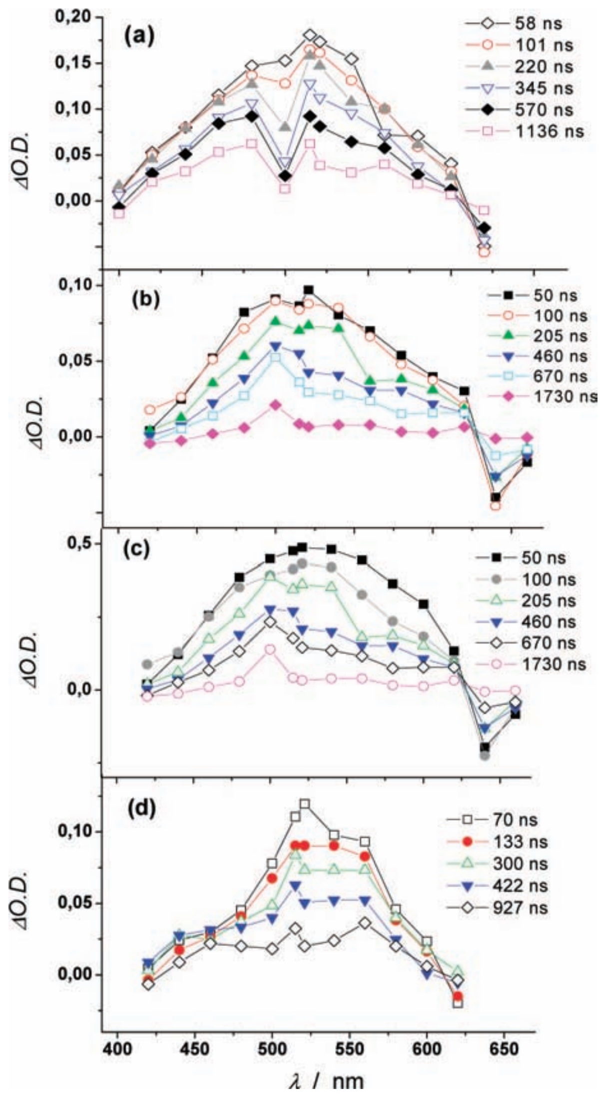

Figure 7. Transient visible spectra of (a) *t*-$Bu_4PcInCl$ (**1**), (b) (*t*-$Bu_2PhO)_4PcInBr$ (**2**), (c) (*t*-$Bu_2PhO)_4PcInI$ (**3**), and (d) $EHO_8PcInTFA$ (**4**) in toluene at different times from excitation (t = 0 s). F_{in} = (a) 0.37, (b) 0.28, (c) 1.31, and (d) 0.37 J cm^{-2}.

first excited triplet state, and second excited triplet state, respectively. σ_0, σ_1, k_{ISC}, τ_{S1}, and τ_{T2} are the ground-state absorption cross section, excited triplet state absorption cross section, intersystem crossing rate, lifetime of the first excited singlet state, and lifetime of the second excited triplet state, respectively. I_{in} indicates the input intensity (in photons cm^{-2} s^{-1}) of the pulses with a Gaussian temporal profile and a top hat spatial profile, as experimentally found. The optimization of the fitting parameters, not available from experiments, i.e., σ_1, k_{ISC}, τ_{S1}, and τ_{T2} (Figure 1), has been accomplished numerically.[23] Experimental data of nonlinear transmittance (Figure 5) have been fitted (Figure 8) with the parameters values listed in Table 3.

The same experimental data and their fitting curves are reported in Figure 8, parts a and b, as transmittance T (= F_{out}/F_{in}) versus log(F_{in}) and F_{out} versus F_{in}, respectively. The double representation of nonlinear transmission data is useful since Figure 8, parts a and b, shows better the quality of the fitting in the low and high fluence regimes, respectively. The fitting shows that the sequential two-photon model is valid for the interpretation of the nonlinear transmittance data of **1**−**4**. In the sole case of **4** the lack of overlap with the sequential two-photon model at high fluences (see Figure 8b) indicates that some other mechanisms are active for this molecule above 0.6 J cm^{-2}. Usually, more than one-photon absorption from excited states becomes active at high fluences in those cases where nonlinear absorption is low.[21a] Further experiments are needed to understand if this is actually the case for phthalocyanine **4**. On the other hand, the discrepancy between calculated values and experimental points in the high-fluence regime of the complex **2** with axial bromide can be related to some degradation of this highly absorbing compound. From Table 3 one finds that the triplet excited-state cross sections of the halogenated axial ligands do not show a strong dependence on the nature of the halogen, and a relatively larger value is found for the nonhalogenated system **4**. More remarkable and important is the variation of the intersystem crossing rate constant k_{ISC} which determines the triplet population and, consequently, the absorp-

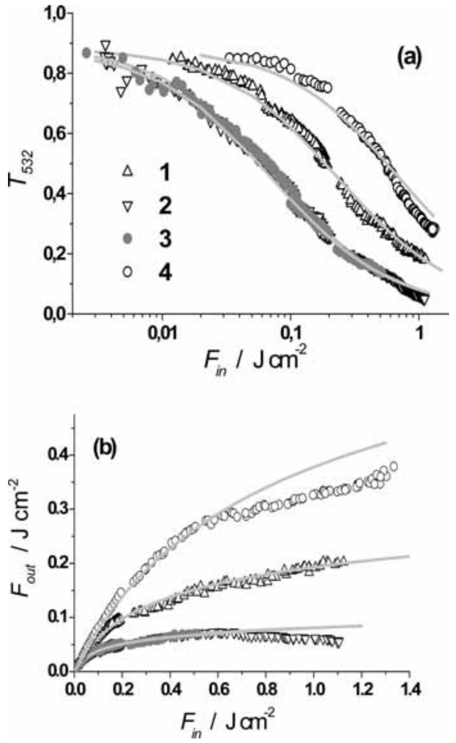

Figure 8. Fitting of (a) T_{532} vs F_{in} and (b) F_{out} vs F_{in} for *t*-$Bu_4PcInCl$ (**1**), (*t*-$Bu_2PhO)_4PcInBr$ (**2**), (*t*-$Bu_2PhO)_4PcInI$ (**3**), and $EHO_8PcInTFA$ (**4**) in toluene irradiated with nanosecond pulses at 532 nm. Fitting curves (continuous gray lines) have been calculated with the multiphoton absorption model depicted in Figure 1 using the values of parameters reported in Table 3.

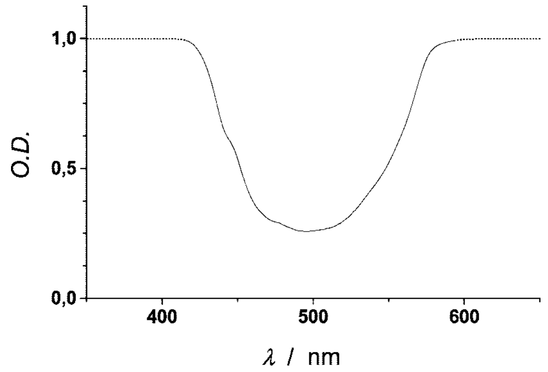

Figure 9. Optical density (OD) of *t*-$Bu_4PcInCl$ (**1**) in polystyrene (film thickness: 0.4 mm).

TABLE 3: Values of Excited Triplet State Absorption Cross Section at 532 nm [$\sigma_1(532)$], Intersystem Crossing Rate (k_{ISC}), Lifetime of the First Excited Singlet State (τ_{S1}), and Lifetime of the Second Excited Triplet State (τ_{T2}) for Indium Pcs 1−4 in Toluene

compound	$\sigma_1(532)$/cm^2	k_{ISC}/s^{-1}	τ_{S1}/s	τ_{T2}/s
t-Bu$_4$PcInCl (**1**)	1.49×10^{-16}	4.3×10^{11}	5.1×10^{-13}	1.0×10^{-13}
(t-Bu$_2$PhO)$_4$PcInBr (**2**)	1.3×10^{-16}	2.2×10^{12}	8.0×10^{-13}	1.0×10^{-13}
(t-Bu$_2$PhO)$_4$PcInI (**3**)	1.33×10^{-16}	2.2×10^{12}	8.0×10^{-13}	1.0×10^{-13}
EHO$_8$PcInTFA (**4**)	7.15×10^{-16}	6.0×10^{10}	2.1×10^{-13}	1.1×10^{-14}

tion activity of this state. The intersystem crossing rates k_{ISC} (Table 3) obtained from the fittings are comprised in the range of $0.6 < k_{ISC} < 22 \times 10^{11}$ s^{-1} for Pcs **1−4**. These values are very close to those experimentally found for similar indium complexes in analogous conditions.[3e,4i,7e] The highest rates ($\approx 10^{12}$ s^{-1}) are found with compounds **2** and **3**, i.e., those complexes that possess axial ligands with the highest mass, namely, Br and I. This is a clear consequence of the heavy-atom effect which accelerates the transfer of excitation from the singlet to the triplet manifold.[24] Therefore, we find a direct correlation between F_{lim}, i.e. a parameter of OPL effectiveness (Table 1), and the rate of intersystem crossing (Table 3) within the series of complexes **1−4**. Under these circumstances it appears much more critical the capability of populating the excited triplet state T_1 with respect to the magnitude of excited triplet absorption cross section σ_1 for the determination of the OPL properties in PcInXs **1−4**.

Photophysical Properties of 1 in Polystyrene. The inclusion of OPL-active materials in solid matrices[3b,9d,25] is very important for the realization of OPL devices useful for practical applications.[2a] We have dispersed t-Bu$_4$PcInCl (**1**) in polystyrene (PS) by codissolution in chloroform. Upon solvent removal at a controlled evaporation rate an optically homogeneous and uniform film can be obtained.[9d] The absorption spectrum of t-Bu$_4$PcInCl (**1**) in PS (0.4 mm thick film) is shown in Figure 9.[17]

The film with PcInX **1** was irradiated with nanosecond laser pulses at 532 nm in order to observe possible nonlinear optical phenomena. The induced changes of optical transmittance for **1** in PS are shown in Figure 10.

Nonlinear transmission of Pc **1** in PS (Figure 10) is characterized by a fast decrease when incident fluence is lower than 0.025 J cm^{-2}. Above this threshold nonlinear transmission changes at a slower rate and shows a quasi stationary behavior. These two different regimes of nonlinear transmission can be attributed to the excited-state absorption of t-Bu$_4$PcInCl (**1**) when $F_{in} <$ 0.025 J cm^{-2}, and to the light-induced modification of polymer for $F_{in} >$ 0.025 J cm^{-2}. In the high-fluence regime, i.e., $F_{in} >$ 0.025 J cm^{-2}, the increase of F_{in} leads to the formation of opaque spots with a milky appearance in correspondence of the irradiated area. Probably, this derives from local overheating due to the nonlinear optical absorption of Pc **1**. These spots are surrounded by radial crevices of the PS film, and onset of pits formation can be observed with the progress of the experiment. The limiting threshold of Pc **1** in PS is approximately 0.025 J cm^{-2} almost in correspondence of the onset of sample degradation. Fitting of the nonlinear transmission curve preceding film damage (Figure 11) has been attempted with the same model used for the description of the nonlinear optical behavior of PcInXs **1−4** in solution (Figure 1, eqs 1a−1d), using $\sigma_0(532) = 3.1 \times 10^{-18}$ cm^2 (Table 2) for t-Bu$_4$PcInCl (**1**) also in PS. The calculated curve (Figure 11) has been produced with the following values of free parameters: $\sigma_1 = 6.36 \times 10^{-16}$ cm^2; $k_{isc} = 3.55 \times 10^{11}$ s^{-1}; $\tau_{S1} = 3.51 \times 10^{-13}$ s; $\tau_{T1} = 3.33 \times 10^{-5}$ s; $\tau_{T2} = 3.33 \times 10^{-14}$ s. The fitting and the parameter values show that the absorption from the excited triplet state is a good model also for **1** in PS although the dynamics of the polymer, which is evident above 0.025 J cm^{-2}, could have some influence also below this fluence.

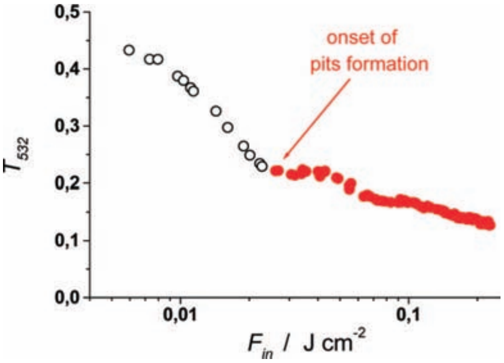

Figure 10. Nonlinear transmittance at 532 nm, T_{532}, for t-Bu$_4$PcInCl (**1**) in polystyrene (film thickness: 0.4 mm). F_{lim}: 0.025 J cm^{-2}. Pc **1** was excited at 532 nm with nanosecond pulses.

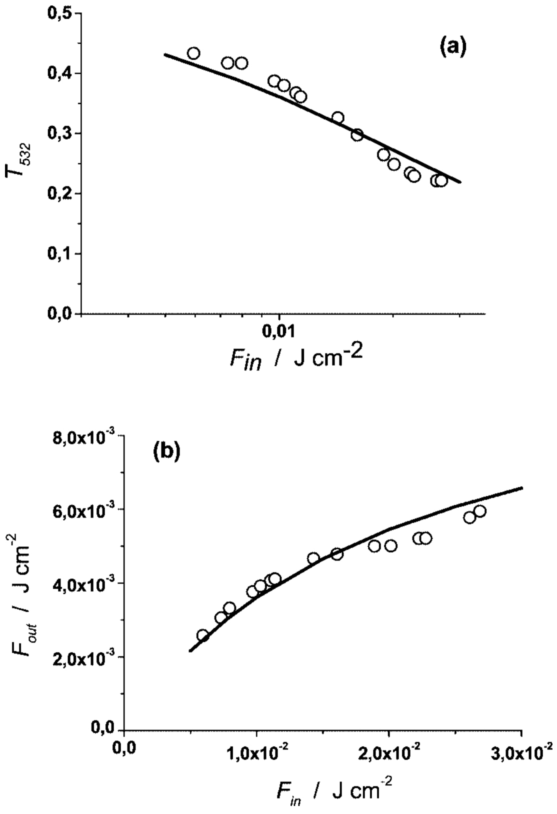

Figure 11. Fitting of (a) T_{532} vs F_{in} and (b) F_{out} vs F_{in} for t-Bu$_4$PcInCl (**1**) in PS film (thickness: 0.4 mm). Polymeric sample was irradiated with nanosecond pulses at 532 nm. Fit (continuous lines) has been created with the multiphoton absorption model depicted in Figure 1. Values of parameters are reported in the text.

Conclusions

Axially substituted indium phthalocyanines 2,(3)-tetra-*tert*-butyl-phthalocyaninato indium chloride (**1**), 2,(3)-tetra-[(3,5-di-*tert*-butyl)-phenyloxy]-phthalocyaninato indium bromide (**2**), 2,(3)-tetra-[(3,5-di-*tert*-butyl)-phenyloxy]-phthalocyaninato indium iodide (**3**), and 2,3-octa-[(2-hexyl)-ethyloxy]-phthalocyaninato indium trifluoroacetate (**4**) have been synthesized in order to determine the influence of the axial ligand on the relevant photophysical properties (linear absorption, emission, nonlinear transmission of nanosecond light pulses, excited-state spectrum) of these indium complexes. Phthalocyanines **1**−**4** exhibit similar linear absorption properties and analogous features of fluorescent emission. However, relevant differences have been observed for their nonlinear absorption properties using nanosecond pulses at 532 nm. Model interpretation of the nonlinear transmission data showed that axial ligands mainly affect the kinetics of excited (triplet) state formation and, in much less extent, its lifetime and spectral properties. We also found that heavier axial ligands (Br and I in complexes **2** and **3**, respectively) induce the larger triplet population and, therefore, the larger variations of nonlinear transmission down to very low values. Nonlinear transmission properties of **1** in PS film have been also evaluated at 532 nm. We found that the model for the dynamic of excited states is always that of a sequential two-photon absorption involving the triplet state, but the dynamic range of the thin film sample is limited by the stability of the host matrix.

Acknowledgment. Financial support from the EU (contracts HPRN-CT-2000-00020 and HPRN-CT-2002-00323) and Italian Ministry of Research and University (PRIN no. 2006034372) are gratefully acknowledged. Dr. Guo Ying Yang from DSO (Singapore) is acknowledged for profitable discussions.

References and Notes

(1) (a) Goutermann, M. In *The Porphyrins*; Dolphin, R., Ed.; Academic Press: New York, 1977; Vol. 3, p 1. (b) Stillman, M. J.; NyokongT. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. J. P., Eds.; VCH: Weinheim, Germany, 1989; Vol. 1, p 133. (c) Lever, A. B. P.; Pickens, S. R.; Minor, P. C.; Licoccia, S.; Ramaswamy, B. S.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800.

(2) (a) Tutt, L. W.; Boggess, T. F. *Prog. Quantum Electron.* **1993**, *17*, 299. (b) Blau, W.; Byrne, H.; Dennis, W. M.; Kelly, J. M. *Opt. Commun.* **1985**, *56*, 25. (c) Band, B. Y. *J. Chem. Phys.* **1985**, *83*, 5453. (d) Hercher, M. *Appl. Opt.* **1967**, *6*, 947.

(3) (a) Shirk, J. S.; Pong, R. G. S.; Bartoli, F. J.; Snow, A. W. *Appl. Phys. Lett.* **1993**, *63*, 1880. (b) Perry, J. W.; Mansour, K.; Lee, I. Y. S.; Wu, X. L.; Bedworth, P. V.; Chen, C. T.; Ng, D.; Marder, S. R.; Miles, P.; Wada, T.; Tian, M.; Sasabe, H. *Science* **1996**, *273*, 1533. (c) Hughes, S.; Spruce, G.; Wherrett, B. S.; Kobayashi, T. *J. Appl. Phys.* **1997**, *81*, 5905. (d) Pittman, M.; Plaza, P.; Martin, M. M.; Meyer, Y. H. *Opt. Commun.* **1998**, *158*, 201. (e) Shirk, J. S.; Pong, R. G. S.; Flom, S. R.; Heckmann, H.; Hanack, M. *J.Phys. Chem. A* **2000**, *104*, 1438. (f) Dini, D.; Calvete, M. J. F.; Hanack, M.; Chen, W.; Ji, W. *ARKIVOC* **2006**, *3*, 77.

(4) (a) De la Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723. (b) O'Flaherty, S. M.; Hold, S. V.; Cook, M. J.; Torres, T.; Chen, Y.; Hanack, M.; Blau, W. J. *Adv. Mater.* **2003**, *15*, 19. (c) Senge, M. O.; Fazekas, M.; Notaras, E. G. A.; Blau, W. J.; Zawadzka, M.; Locos, O. B.; Mhuircheartaigh, E. M. N. *Adv. Mater.* **2007**, *19*, 2737. (d) De la Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. *J. Mater. Chem.* **1998**, *8*, 1671. (e) Nalwa, H. S.; Shirk, J. S. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. J. P., Eds.; VCH: Weinheim, Germany, 1996; Vol. 4, p 79. (f) Dini, D.; Barthel, M.; Hanack, M. *Eur. J. Org. Chem.* **2001**, 3759. (g) Hanack, M.; Dini, D.; Barthel, M.; Vagin, S. *Chem. Rec.* **2002**, *2*, 129. (h) Calvete, M.; Yang, G. Y.; Hanack, M. *Synth. Met.* **2004**, *141*, 231. (i) Perry, J. W. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; p 813. (j) Dini, D.; Yang, G. Y.; Hanack, M. In *Targets in Heterocyclic Systems. Chemistry and Properties*; Attanasi, A. O., Spinelli, D., Eds.; Societa' Chimica Italiana: Rome, 2004; Vol. 8, p 1.

(5) (a) Brzozowski, L.; Sargent, E. H. *J. Opt. Soc. Am. B* **2000**, *17*, 1360. (b) Kovsh, D. I.; Yang, S.; Hagan, D. J.; Van Stryland, E. W. *Appl. Opt.* **1999**, *38*, 5168. (c) Chapple, P. B.; Hermann, J. A.; McDuff, R. G. *Opt. Quantum Electron.* **1999**, *31*, 555.

(6) (a) Hanack, M.; Heckmann, H.; Polley, R. In *Methods of Organic Chemistry (Houben-Weyle-Hetarenes IV: Six-Membered and Larger Heterorings with Maximum Insaturation)*; Schaumann, E., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1997; Vol. 9, p 717. (b) McKeown, N. B. In *Science of Synthesis (Houben-Weyle, Methods of Molecular Transformations-Hetarenes and Related Ring Systems)*; Weinreb, S. M., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 2004; Vol. 17, p 1237. (c) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *27*, 27. (d) Dini, D.; Hanack, M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Elsevier Science: Amsterdam, The Netherlands, 2003; Vol. 17, p 1. (e) Dini, D.; Hanack, M. *J. Porphyrins Phthalocyanines* **2004**, *8*, 915.

(7) (a) Yang, G. Y.; Hanack, M.; Lee, Y. W.; Dini, D.; Pan, J. F. *Adv. Mater.* **2005**, *17*, 875. (b) Dini, D.; Yang, G. Y.; Hanack, M. *J. Chem. Phys.* **2003**, *119*, 4857. (c) Yang, G. Y.; Hanack, M.; Lee, Y. W.; Chen, Y.; Lee, M. K. Y.; Dini, D. *Chem. Eur. J.* **2003**, *9*, 2758. (d) Barthel, M.; Dini, D.; Vagin, S.; Hanack, M. *Eur. J. Org. Chem.* **2002**, 3756. (e) Hanack, M.; Schneider, T.; Barthel, M.; Shirk, J. S.; Flom, S. R.; Pong, R. G. S. *Coord. Chem. Rev.* **2001**, *219*−*221*, 235. (f) Dini, D.; Calvete, M. J. F.; Hanack, M.; Pong, R. G. S.; Flom, S. R.; Shirk, J. S. *J. Phys. Chem. B* **2006**, *110*, 12230. (g) Maya, E. M.; Snow, A. R.; Shirk, J. S.; Pong, R. G. S.; Flom, S. R.; Roberts, G. L. *J. Mater. Chem.* **2003**, *13*, 1603. (h) Vagin, S.; Yang, G. Y.; Lee, M. K. Y.; Hanack, M. *Opt. Commun.* **2003**, *228*, 119. (i) Sun, W.; Wang, G.; Li, Y.; Calvete, M. J. F.; Dini, D.; Hanack, M. *J. Phys. Chem. A* **2007**, *111*, 3263.

(8) (a) Coulter, D. R.; Miskowski, V. M.; Perry, J. W.; Wei, T. H.; Van Stryland, E. W.; Hagan, D. J. *Proc. SPIE*−*Int. Soc. Opt. Eng.* **1989**, *1105*, 42. (b) Chen, Y.; Subramanian, L. R.; Fujitsuka, M.; Ito, O.; O'Flaherty, S.; Blau, W. J.; Schneider, T.; Dini, D.; Hanack, M. *Chem. Eur. J.* **2002**, *8*, 4248. (c) Chen, Y.; Dini, D.; Hanack, M.; Fujitsuka, M.; Ito, O. *Chem. Commun.* **2004**, 340. (d) Youssef, T. E.; O'Flaherty, S.; Blau, W. J.; Hanack, M. *Eur. J. Org. Chem.* **2004**, 101. (e) Calvete, M. J. F.; Dini, D.; Flom, S. R.; Hanack, M.; Pong, R. G. S.; Shirk, J. S. *Eur. J. Org. Chem.* **2005**, 3499. (f) Dini, D.; Hanack, M.; Meneghetti, M. *J. Phys. Chem. B* **2005**, *109*, 12691. (g) Chauke, V.; Durmus, M.; Nyokong, T. *J. Photochem. Photobiol., A* **2007**, *192*, 179.

(9) (a) Perry, J. W.; Mansour, K.; Miles, P.; Chen, C. T.; Marder, S. R.; Kwag, G.; Kenney, M. *Polym. Mater. Sci. Eng.* **1995**, *72*, 222. (b) Perry, J. W.; Mansour, K.; Marder, S. R.; Chen, C. T.; Miles, P.; Kenney, M. E.; Kwag, G. *Mater. Res. Soc. Symp. Proc.* **1995**, *374*, 257. (c) Plater, M. J.; Jeremiah, A.; Bourhill, G. *J. Chem. Soc., Perkin Trans. 1* **2002**, 91. (d) Dini, D.; Barthel, M.; Schneider, T.; Ottmar, M.; Verma, S.; Hanack, M. *Solid State Ionics* **2003**, *165*, 289. (e) O'Flaherty, S. M.; Hold, S. V.; Chen, Y.; Hanack, M.; Blau, W. J. *Proc. SPIE*−*Int. Soc. Opt. Eng.* **2003**, *4991*, 183. (f) Shirk, J. S.; Flom, S. R.; Lindle, J. R.; Bartoli, F. J.; Snow, A. W.; Boyle, M. E. *Mater. Res. Soc. Symp. Proc.* **1994**, *328*, 661.

(10) (a) Li, Y.; Dini, D.; Calvete, M. J. F.; Hanack, M.; Sun, W. *J. Phys. Chem. A* **2008**, *112*, 472. (b) Dini, D.; Hanack, M.; Wei, J.; Weizhe, C. *Mol. Cryst. Liq. Cryst.* **2005**, *431*, 259. (c) Dini, D. *Int. J. Mol. Sci.* **2003**, *4*, 291.

(11) (a) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; p 124. (b) Perry, J. W.; Mansour, K.; Marder, S. R.; Perry, K. J.; Alvarez, D.; Choong, I. *Opt. Lett.* **1994**, *19*, 625.

(12) Vagin, S.; Barthel, M.; Dini, D.; Hanack, M. *Inorg. Chem.* **2003**, *42*, 2683.

(13) (a) Hanack, M.; Heckmann, H. *Eur. J. Inorg. Chem.* **1998**, 367. (b) Mikhalenko, S. A.; Barkanova, S. V.; Lebedev, O. L.; Lukyanets, E. A. *Zh. Obshch. Khim.* **1971**, *41*, 2735.

(14) Tolbin, A. Y.; Ivanov, A. V.; Tomilova, L. G.; Zefirov, N. S. *Mendeleev Commun.* **2002**, *12*, 96.

(15) (a) Woehrle, D.; Eskes, M.; Shigehara, K.; Yamada, A. *Synthesis* **1993**, 194. (b) Woehrle, D.; Schnurpfeil, G.; Knothe, G. *Dyes Pigm.* **1992**, *18*, 91.

(16) (a) Lyubimtsev, A.; Vagin, S.; Syrbu, S.; Hanack, M. *Eur. J. Org. Chem.* **2007**, 2000. (b) Agirtas, M. S. *Dyes Pigm.* **2007**, *74*, 490. (c) Plater, M. J.; Jeremiah, A.; Bourhill, G. *J. Chem. Soc., Perkin Trans. 1* **2002**, 91. (d) Vagin, S.; Frickenschmidt, A.; Kammerer, B.; Hanack, M. *Eur. J. Org. Chem.* **2005**, 3271.

(17) (a) Snow, A. W. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Elsevier Science: Amsterdam, The Netherlands, 2003; Vol. 17, p 129. (b) Snow, A. W.; Jarvis, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 4706.

(18) Dini, D.; Hanack, M.; Egelhaaf, H. J.; Sancho-Garcia, J. C.; Cornil, J. *J. Phys. Chem. B* **2005**, *109*, 5425.

(19) Bonnett, R.; Harriman, A.; Kozyrev, A. N. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 763.

(20) (a) Pau, H.; Chen, W.; Feng, Y. P.; Ji, W.; Lin, J. *Appl. Phys. Lett.* **2006**, *88*, 223106. (b) Fu, S.; Zhu, X.; Wong, W. Y.; Ye, C.; Wong, W. K.; Li, Z. *Eur. J. Inorg. Chem.* **2007**, 2004. (c) Vincent, D. *Appl. Opt.* **2001**, *40*, 6646.

(21) (a) Dini, D.; Calvete, M. J. F.; Hanack, M.; Amendola, V.; Meneghetti, M. *Chem. Commun.* **2006**, 2394. (b) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501.

(22) (a) Giuliano, C. R.; Hess, L. D. *IEEE J. Quantum Electron.* **1967**, *3*, 358. (b) Sutherland, R. L.; McLean, D. G.; Kirkpatrick, S. M.; Fleitz, P. A.; Chandra, S. Brant, M. C. In *Multiphoton and Light Driven Multielectron Processes in Organics: New Phenomena, Materials and Applications*; Kajzar, F., Agranovich, M. V., Eds.; Kluwer: Amsterdam, The Netherlands, 2000; p 67.

(23) Ehlert, J.; Stiel, H.; Teuchner, K. *Comput. Phys. Commun.* **2000**, *124*, 330.

(24) (a) Lower, S. K.; El-Sayed, M. A. *Chem. Rev.* **1966**, *66*, 199. (b) Kearns, D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087. (c) Marchetti, A. P.; Kearns, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 768.

(25) (a) Xia, T. J.; Hagan, D. J.; Dogariu, A.; Said, A. A.; Van Stryland, E. W. *Appl. Opt.* **1997**, *36*, 4110. (b) Nagamura, T.; Naito, A.; Yoshida, I.; Chen, Y.; Hanack, M. *J. Nonlinear Opt. Phys. Mater.* **2002**, *11*, 205. (c) Fuqua, P. D.; Mansour, K.; Alvarez, D.; Marder, S. R.; Perry, J. W.; Dunn, B. *Proc. SPIE—Int. Soc. Opt. Eng.* **1992**, *1758*, 499. (d) Brant, M. C.; De Rosa, M. E.; Jiang, H.; McLean, D. G.; Sutherland, L.; Campbell, A. L. *Proc. SPIE—Int. Soc. Opt. Eng.* **1992**, *1758*, 499. (e) Mansour, K.; Fuqua, P.; Marder, S. R.; Dunn, B.; Perry, J. W. *Proc. SPIE—Int. Soc. Opt. Eng.* **1994**, *2143*, 239.

JP802960S