

Synthesis of axially substituted gallium, indium and thallium phthalocyanines with nonlinear optical properties

Danilo Dini^a, Mario J.F. Calvete^a, Michael Hanack^{a*}, Weizhe Chen^b, and Wei Ji^b

^a*Institute of Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany, and*

^b*Department of Physics, National University Singapore, Science Drive 4, 117542 Singapore*
E-mail: hanack@uni-tuebingen.de

Dedicated to Professor Jim Coxon on the occasion of his 65th birthday

Abstract

Axially substituted phthalocyanines with gallium, indium and thallium as central coordinated atoms have been synthesized for nonlinear optical (NLO) studies. In particular, the optical limiting effect of 2(3)-tetrabutylphthalocyaninato indium chloride (**1**), hexadecachlorophthalocyaninato indium chloride (**2**), 2,3-octa-(2-ethyl-hexyloxy) phthalocyaninato gallium chloride (**3a**), 2,3-octa-(2-ethyl-hexyloxy)phthalocyaninato indium chloride (**3b**), 2,3-octa-(2-ethyl-hexyloxy)phthalocyaninato indium trifluoroacetate (**4a**), 2,3-octa-(2-ethyl-hexyloxy)-phthalocyaninato thallium trifluoroacetate (**4b**), and 2,3,9,10,16,17-hexa-(2-ethyl-hexyloxy) monobenzophthalocyaninato indium chloride (**5**) has been evaluated and compared when the NLO regime was determined by nanosecond laser pulses in the visible spectrum. In the case of complexes **1** and **4a** the determination of the excited state absorption cross section at 532 nm could be possible due the verification of reversible saturation of NLO absorption in the adopted experimental conditions. This allowed the use of the steady-state solutions for the kinetic equations describing sequential multiphoton absorption.

Keywords: Phthalocyanine, dinitrile, aromaticity, axial substitution, nonlinear optics, optical limiting

Introduction

Phthalocyanines¹ (Pcs) are chemically stable complexes whose ligand is characterized by the presence of forty aromatic π -electrons as a summation of the ten aromatic electrons which are present in each of the four isoindoline units (Figure 1). Different from porphyrins the four isoindoline units of Pcs are bridged by four *meso* nitrogen atoms, which allow the further

electronic conjugation between the isoindoline units. The presence of such an extended network of conjugated π -electrons imparts several properties of interest in Pc molecules. In particular, strong optical absorption in the visible spectrum,² electrical conductivity,³ photoconductivity⁴ and nonlinear optical (NLO) properties⁵ combined with the chemical robustness of Pcs render this class of compounds particularly suitable for several practical applications like dyes or pigments,⁶ gas sensing,⁷ xerographic reproduction,^{4c} or optical limiting (OL)⁸ among others.⁹

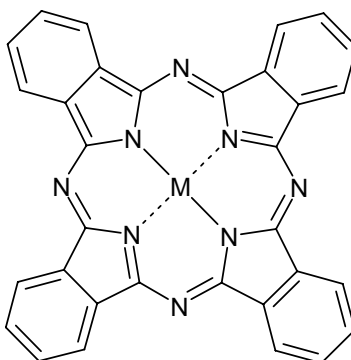


Figure 1. Phthalocyanine. M can be any bivalent atom of the periodic table or a bivalent chemical group.

In particular, Pcs and analogs are receiving nowadays a considerable interest as active materials for OL devices for their capability of absorbing intense radiations (in the order of several megawatts per square meter), in the vis/NIR spectral range in a reversible fashion with no severe modifications of their optical and chemical properties.^{8,10} These characteristics of Pcs and analogs (Figure 1) 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).¹¹ When excited state absorption occurs from a triplet excited state the related OL effect can be furtherly improved in Pcs through the coordination of heavy central atoms, e.g. Pb,^{10a} In^{10b,10c} or Tl,¹² which accelerate intersystem crossing (ISC) by means of spin-orbit coupling in the excited complex. Under these conditions the absorbing triplet level can be populated at high rates and yields.¹³

Another favourable feature of these complexes for OL purposes is their capability of hosting tri- or tetravalent central atoms that require the further coordination of one and two axial substituents, respectively.¹⁴ In fact, axial substituents indirectly stabilize the electronic excited states which are involved in the multiphoton absorption processes through either preventing or reducing intermolecular aggregation in solution with the increase of molecules concentration.^{10c} In the event of excited state absorption the occurrence of molecular aggregation should be avoided since it perturbs the electronic structure of the complex in the non-aggregated form,¹⁵ and generally decreases the lifetime of excited states due to self-quenching.¹⁶ From this it is evident that new Pc structures with improved OL effect would coordinate heavy atoms with large axial substituents in order to afford both occurrence of the heavy-atom effect and prevention of

molecular aggregation. For these reasons we have synthesized the series of axially substituted phthalocyaninato gallium, indium and thallium complexes **1-5** (Figure 2), whose structures combine the presence of large central atoms and axial ligands, in order to analyze and compare the OL effect produced by these complexes.

In particular we prepared 2(3)-tetratertbutylphthalocyaninato indium chloride (*t*Bu₄PcInCl) (**1**);^{10b} hexadecachlorophthalocyaninato indium chloride (Cl₁₆PcInCl) (**2**); 2,3-octa-(2-ethyl-hexyloxy)phthalocyaninato gallium chloride [(EHO)₈PcGaCl] (**3a**); 2,3-octa-(2-ethyl-hexyloxy)phthalocyaninato indium chloride [(EHO)₈PcInCl] (**3b**); 2,3-octa-(2-ethyl-hexyloxy)phthalocyaninato indium trifluoroacetate [(EHO)₈PcIn(OCOCF₃)] (**4a**); 2,3-octa-(2-ethyl-hexyloxy)phthalocyaninato thallium trifluoroacetate [(EHO)₈PcTl(OCOCF₃)] (**4b**); and 2,3,9,10,16,17-hexa-(2-ethyl-hexyloxy)monobenzophthalocyaninato indium chloride [(EHO)₆PhPcInCl] (**5**) (Figure 2). The role of the central metal as well as the effect of the axial substituents on the resulting NLO properties are discussed. The evaluation of the NLO transmission for the complexes **1-5** has been carried out for ns pulses at 532 nm.

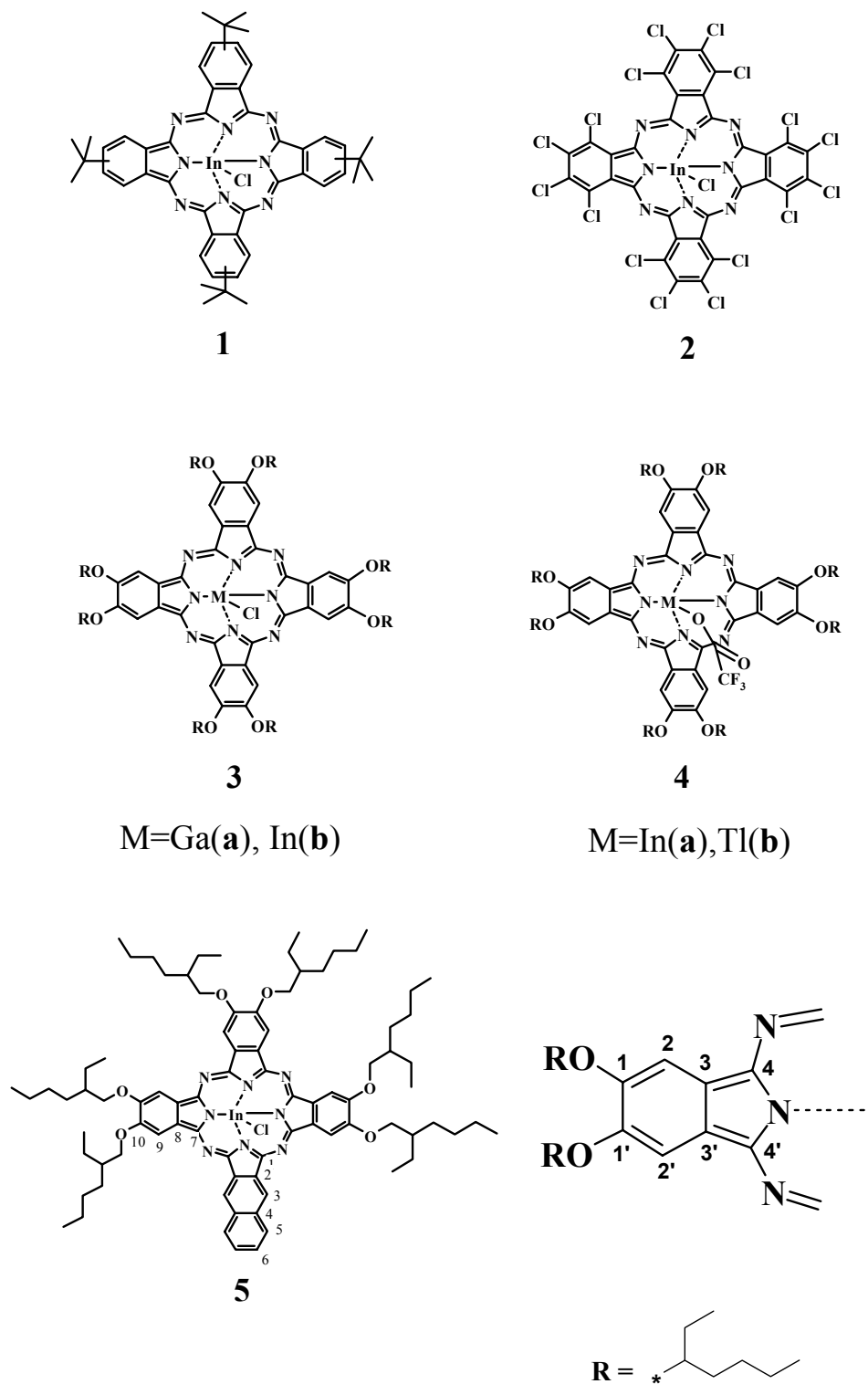


Figure 2. Axially substituted gallium (**3a**), indium (**1,2,3b,4a,5**) and thallium (**4b**) phthalocyanines for NLO studies. Notation for the identification of the atoms in the ligands **1-4** is given in the sketched isoindolinine unit.

Results and Discussion

Axially substituted phthalocyanines **1-5** (Figure 2) all display reverse saturable absorption (RSA)¹⁷ when irradiated with ns pulses at 532 nm within the incident fluence (F_{in}) range $5 \times 10^{-3} < F_{in} < 3 \text{ J cm}^{-2}$ (Figures 3-6). This implies that the optical transmission of the solutions of these complexes reversibly decreases with the increase of F_{in} when the radiation fluence is in the order of 10^{16} - 10^{19} photons per ns. The occurrence of such a NLO effect at 532 nm is mainly attributed to a mechanism of sequential two-photon absorption (Figure 7), which involves the participation of an excited state of the complex in the process of multiphoton absorption.¹⁸ Under these circumstances an excited electronic state is formed upon absorption of the first photon, and it absorbs more efficiently than the ground state at the wavelength of irradiation.^{10,17-19} In terms of absorption cross-section σ the occurrence of RSA in **1-5** brings about the existence of excited states which have the absorption cross-section σ_{exc} larger than the ground state, i.e. $\sigma_{exc} > \sigma_g$.²⁰ Since incident light pulses have a duration of several ns (broad pulse duration range: 3-10 ns), the lifetime of the absorbing excited state of Pcs **1-5** cannot be shorter than several ns. There is also another implication in the occurrence of RSA of pulsed radiation from Pcs **1-5** through excited state absorption: the formation time of the absorbing excited states [either via an internal conversion or an intersystem crossing process (ISC), Figure 7] has to be shorter than the pulse duration itself, i.e. less than few ns. In Pcs the effect of RSA upon irradiation with ns long pulses in the visible spectrum is associated with the strong absorption of a triplet excited state.¹⁰ This is because ISC usually takes place in less than 1 ns in Pcs¹⁰ and the presence of heavy atoms like Ga, In and Tl in **1-5** tends to further accelerate such a process.²¹

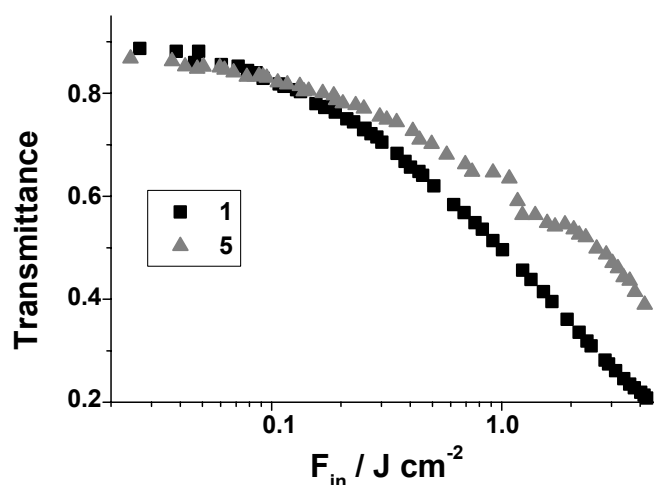


Figure 3. Variation of the NLO transmittance with the input fluence F_{in} for *t*Bu₄PcInCl (**1**) and unsymmetrically substituted (EHO)₆PhPcInCl (**5**) at 532 nm. Laser pulse duration was 7 ns. The concentrations of **1** (in toluene) and **5** (in pyridine) were 0.07 and 0.09 g L⁻¹, respectively. These values correspond to the concentrations 8 and 6x10⁻⁵M for **1** and **5**, respectively. The linear transmittance T_0 of the samples was 0.88. The beam waist of the focused laser is about 40 μm and 1 mm-thick cell was used for this experiment.

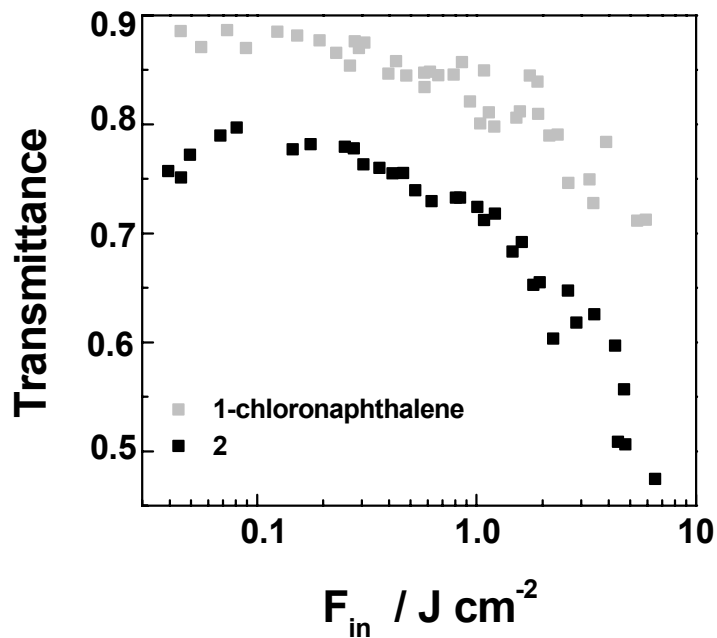


Figure 4. Variation of the NLO transmittance with the input fluence F_{in} for a saturated solution of $Cl_{16}PcInCl$ (**2**) in 1-chloronaphthalene at 532 nm. Laser pulse duration was 7 ns. The linear transmittance T_0 of the samples was 0.78. The beam waist of the focused laser is about 40 μm and 1 mm-thick cell was used for this experiment.

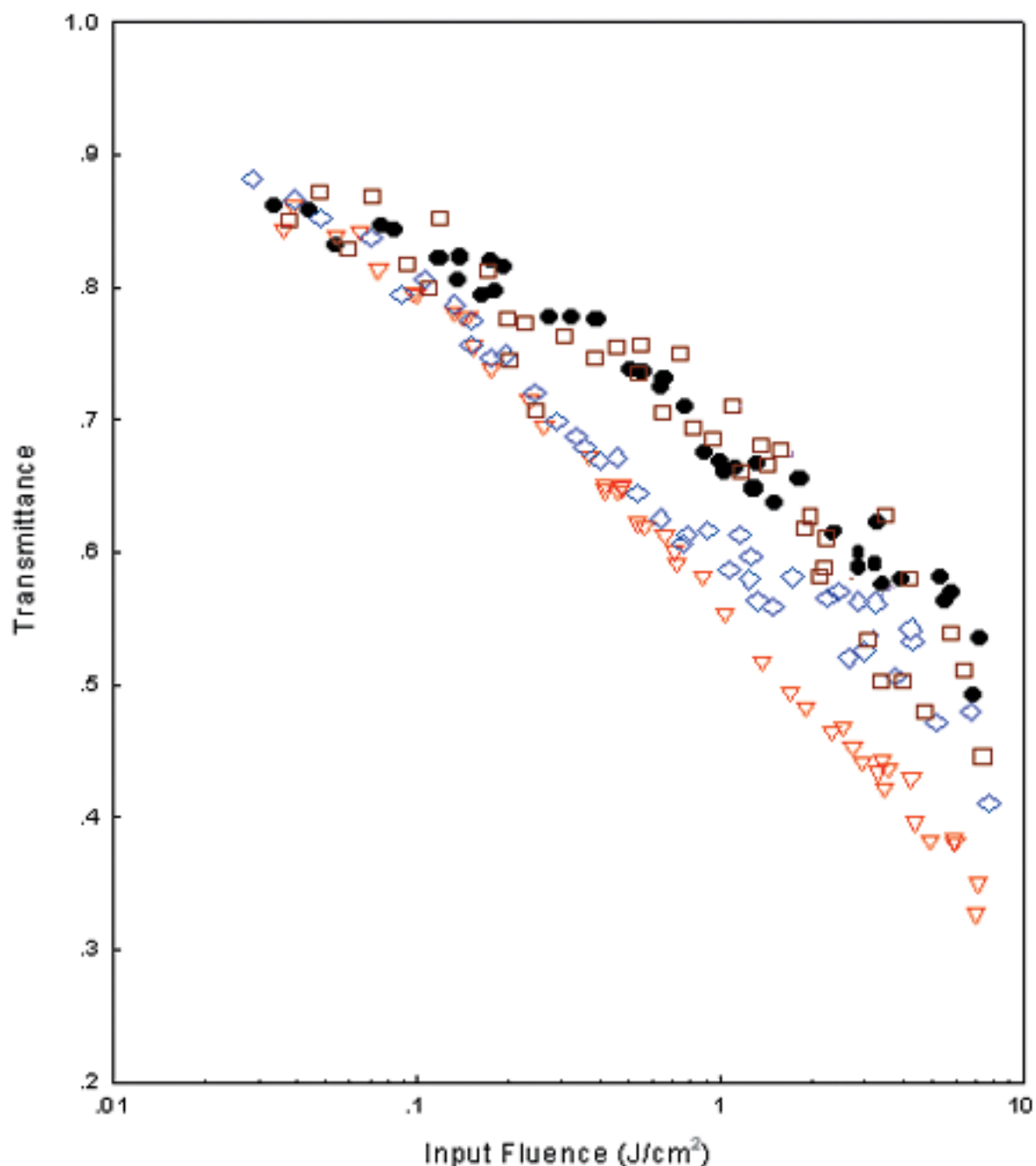


Figure 5. Variation of the NLO transmittance at 532 nm with F_{in} for $(EHO)_8PcGaCl$ (**3a**, open down triangles), $(EHO)_8PcInCl$ (**3b**, \diamond), $(EHO)_8PcTi(OCOCF_3)$ (**4b**, \square) and C_{60} for comparison (\bullet). Laser pulse duration was 7 ns. The concentrations of **3a**, **3b** and **4b** in toluene are 0.8, 0.2 and 0.3 g L⁻¹, respectively. These values correspond to the concentrations 4.8×10^{-4} , 1.2×10^{-4} and 1.6×10^{-4} M for **3a**, **3b** and **4b**, respectively. The linear transmittance T_0 of the samples was the same for all the complexes ($T_0 = 0.86$). The beam waist of the focused laser is about 40 μm and 1 mm-thick cell was used for this experiment.

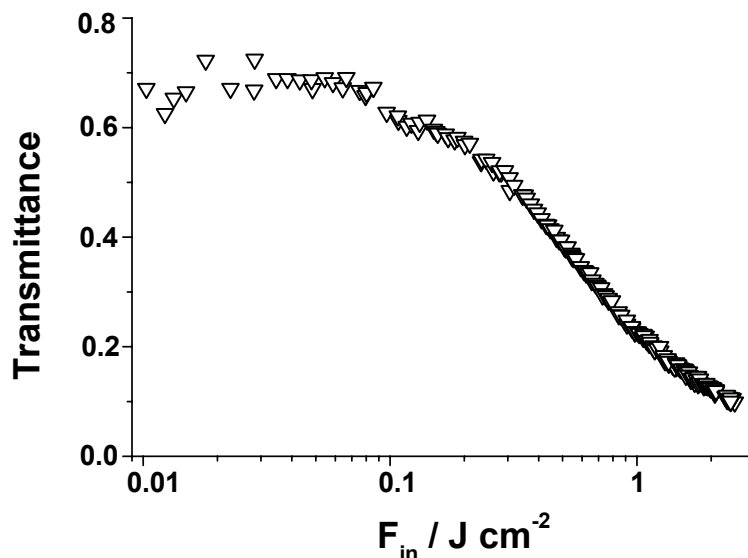


Figure 6. Variation of the NLO transmittance at 532 nm with F_{in} for $(EHO)_8PcIn(OCOCF_3)$ (**4a**). Laser pulse duration was 7 ns. The concentration of **4a** in toluene is 2.6×10^{-4} M. The linear transmittance T_0 of the sample at the wavelength of analysis was 0.72. The beam waist of the focused laser is about 50 μ m and 1 mm-thick cell was used for this experiment.

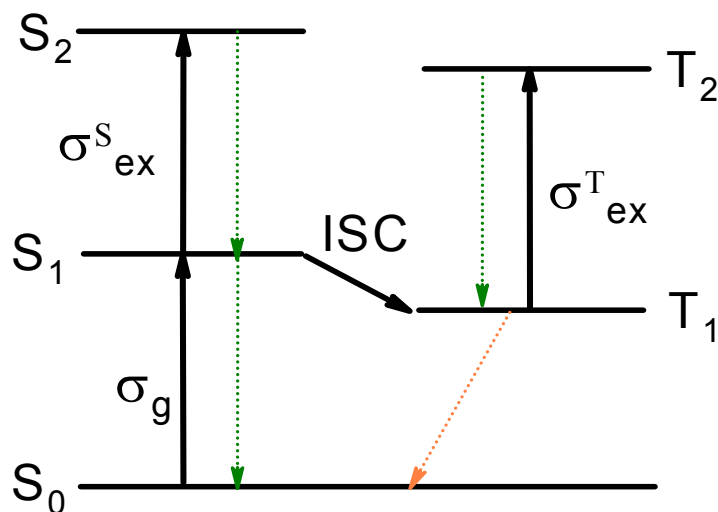


Figure 7. Jablonski diagram depicting the mechanism of sequential two-photon absorption. $S_0, S_{1(2)}$ and $T_{1(2)}$ indicate the ground singlet state, the first (second) excited singlet state and the first (second) excited triplet state, respectively. Pc absorbs the first photon through the transition $[S_0 \rightarrow S_1]$, and, depending on the dynamics of the irradiated system, will absorb sequentially a second photon through either the transition $[S_1 \rightarrow S_2]$ or $[T_1 \rightarrow T_2]$. $\sigma_{ex}^{S(T)}$ and σ_g are the absorption cross-sections from the excited singlet (triplet) state and the ground state, respectively. RSA implies that $\sigma_{ex}^{S(T)} > \sigma_g$. Oblique and straight downward arrows indicate phosphorescence and fluorescence decays, respectively. $[S_1 \rightarrow T_1]$ is intersystem crossing (ISC). Only the fundamental vibrational level of the various electronic levels is indicated.

When the NLO transmission curves of *t*Bu₄PcInCl (**1**) and (EHO)₆PhPcInCl (**5**) are compared (Figure 3), we observe a more rapid decrease of transmittance for **1** with respect to **5** in correspondence of F_{in} values higher than 0.2 J cm⁻². One of the main reasons for such differences in the NLO behaviors of **1** and **5** (Figure 3) has to be found in the diverse nature and number of the peripheral substituents in these complexes, which have distinct capabilities of preventing molecular aggregation in **1** and **5**. It is known that the possible formation of molecular aggregates in Pcs increases the rate of relaxation of excited states due to self-quenching¹⁶ and, consequently, the lifetime of the absorbing excited state of Pcs in NLO regimes decreases. The resulting OL effect due to excited state absorption (Figure 7) is thus reduced upon occurrence of molecular aggregation.^{10c}

From these considerations it is expected that the lifetimes of the absorbing excited state in *t*Bu₄PcInCl (**1**) and (EHO)₆PhPcInCl (**5**) are generally different as well as the extent of the perturbation of the electronic structure of **1** and **5** from their monomeric forms.¹⁶ In particular, the lack of any substituent in the peripheral phenyl ring of unsymmetrical (EHO)₆PhPcInCl (**5**) is a major cause of molecular aggregation in correspondence of such an unsubstituted moiety and the observed smaller OL effect of the unsymmetrical complex **5** (minimum transmittance $T_{min} = 0.42$) with respect to *t*Bu₄PcInCl (**1**) ($T_{min} = 0.2$) is associated with such a structural variation.²² In conclusion, the presence of an unsubstituted moiety in (EHO)₆PhPcInCl (**5**) brings about the destabilization of the first excited triplet state (T_1 in Figure 6) of **5** due to the occurrence of intermolecular interactions in correspondence of such a moiety.²² Moreover, another possible reason for the better OL efficiency of *t*Bu₄PcInCl (**1**) with respect to (EHO)₆PhPcInCl (**5**) is the lower extinction coefficient of **1** with respect to **5** at 532 nm. Such a difference imposes a larger concentration of **1** with respect to **5** in order to obtain the same value of linear transmittance T_0 in both solutions of *t*Bu₄PcInCl (**1**) and (EHO)₆PhPcInCl (**5**). As a consequence of that, the density of the photoactive units is higher for the solution of **1** in comparison to **5** and a stronger NLO absorption of **1** is expected.

In the case of the perchlorinated system Cl₁₆PcInCl (**2**) a generally low OL efficiency at 532 nm (Figure 4) is observed when this is compared to the ones of *t*Bu₄PcInCl (**1**) and (EHO)₆PhPcInCl (**5**) (Figure 3). This trend is expected since **2** has shown clear evidence of molecular aggregation in 1-chloronaphthalene (the solvent used in the experiment of Figure 4), as ascertained by the wide broadening of the optical absorption bands of **2** (not shown here).¹⁵ As a consequence of that, the lifetime of the absorbing excited state of Cl₁₆PcInCl (**2**) is extremely shortened with respect to a non-aggregated system like *t*Bu₄PcInCl (**1**), and the associated OL effect results relatively poor with $T_{min} = 0.5$ (the latter value includes also the NLO contribution of the solvent - see upper curve in Figure 4).

The variation of the NLO transmission of (EHO)₈PcGaCl (**3a**), (EHO)₈PcInCl (**3b**) and (EHO)₈PcTl(OCOCF₃) (**4b**) is presented in Figure 5. The comparison of the OL effect from **3a**, **3b** and **4b** when the linear transmittance T_0 of their solutions is equal ($T_0 = 0.86$ in toluene) shows that the gallium complex (EHO)₈PcGaCl (**3a**) displays the larger limiting effect ($T_{min} = 0.33$), whereas the indium (**3b**) and thallium (**4b**) complexes have a comparable behavior ($T_{min} =$

0.41 and 0.45 for **3b** and **4b**, respectively). Such a trend can be explained considering that different concentrations of the photoactive molecules have been used in order to keep the same value of T_0 at the wavelength of analysis (532 nm). In fact, the comparison of the OL effect at a fixed wavelength imposes the condition of equal T_0 values at that wavelength for the solutions to be compared. The variations of the molar extinction values at 532 nm (ϵ_{532}) for $(\text{EHO})_8\text{PcGaCl}$ (**3a**), $(\text{EHO})_8\text{PcInCl}$ (**3b**), and $(\text{EHO})_8\text{PcTl}(\text{OCOCF}_3)$ (**4b**) in toluene [$\log\{\epsilon_{532}/(\text{L mol}^{-1} \text{cm}^{-1})\} = 3.13, 3.74$ and 3.60 for **3a**, **3b** and **4b**, respectively], require that the amount of substance necessary for reaching a fixed value of T_0 is different. Consequently, the observed variations in the OL effect have to be mostly associated with the differences in the values of concentration of the photoactive units.^{8c}

In case of $(\text{EHO})_8\text{PcInCl}$ (**3b**) and $(\text{EHO})_8\text{PcTl}(\text{OCOCF}_3)$ (**4b**) the similarity of their ϵ_{532} values and, consequently, of their concentration in the OL experiment of Figure 5, allows an additional consideration concerning the comparison of the actual OL effectiveness of **3b** and **4b**. Since $(\text{EHO})_8\text{PcInCl}$ (**3b**) and $(\text{EHO})_8\text{PcTl}(\text{OCOCF}_3)$ (**4b**) reach close values of T_{\min} and have similar values of concentration in the adopted experimental conditions, it is concluded that the ISC acceleration (Figure 7) associated with the heavy-atom effect²¹ is not critically influenced by the nature of the central metal in passing from In to Tl when the process of multiphoton absorption of Pcs involves ns laser pulses.

The variation of the NLO transmittance of $(\text{EHO})_8\text{PcIn}(\text{OCOCF}_3)$ (**4a**) as a function of F_{in} is presented in Figure 6. When the concentration of $(\text{EHO})_8\text{PcIn}(\text{OCOCF}_3)$ (**4a**) is $2.6 \times 10^{-4}\text{M}$, **4a** reaches the value $T_{\min} = 0.1$. Similar to **1** (Figure 3) complex **4a** also shows the onset of the flattening of the NLO transmission curve, which is indicative of the beginning of a saturation process.^{11a} In these conditions the value of T_{\min} corresponds to the saturation transmittance T_{sat} . Saturation onset takes place at $F_{\text{in}} = 4.2$ and 2.4 J cm^{-2} for **1** and **4a**, respectively (Figures 3 and 6), whereas the occurrence of NLO absorption saturation is not verified with **2,5** (Figure 4), **3a,3b** and **4b** (Figure 5) within the same range of F_{in} . When saturation effects are verified in the multiphoton absorption process of a molecular species it is then possible to evaluate the absorption cross section σ_{exc} of the absorber for the excited state transition at the basis of the OL effect.^{11a} In fact, if it is assumed that the initial ground state population density (N_g) is totally transferred into the highly absorbing excited state the value of T_{sat} can be directly correlated with σ_{exc} through the relationship:^{11a}

$$T_{\text{sat}} = \exp(-\sigma_{\text{exc}}N_gL) \quad (1)$$

where L is the optical path length. From eq (1) it is found $\sigma_{\text{exc}} = 3.2 \times 10^{-16}$ and $1.4 \times 10^{-16} \text{ cm}^2$ at 532 nm for $t\text{Bu}_4\text{PcInCl}$ (**1**) and $(\text{EHO})_8\text{PcIn}(\text{OCOCF}_3)$ (**4a**), respectively. In the case of **1** the value of σ_{exc} at 532 nm calculated through eq (1) is comparatively large (about five times larger) with respect to the values previously found for $t\text{Bu}_4\text{PcInCl}$ (**1**).^{8c,10b,10c} This is because in eq (1) it is supposed that T_{sat} is determined exclusively by the molecular absorber when in the excited state with the exclusion of the ground state absorption which precedes the absorption of the

second photon from the excited state (Figure 7). On the other hand, such an approximation can be removed if we consider that the actual value of transmittance T is always determined by all the states (either ground or excited) of the molecule which have a non null value of σ at the wavelength of irradiation and contribute at some stage to the decrease of transmittance.²³ This leads to the definition of the relationship:

$$T = \exp\{-[\sum_i(\sigma_i \cdot N_i)]*L\} \quad (2)$$

where the summation is extended to all the i - states of the molecule (either ground or excited or aggregated with a defined number of absorbing molecular units), which have non-zero absorption cross-section at the wavelength of irradiation. In eq(2) N_i refers to the number of chemically defined entities, either monomolecular or aggregated, which are in a state with absorption cross-section σ_i .

When sequential two-photon absorption takes place and no optically absorbing aggregates are formed eq(2) is simplified into:

$$T = \exp[-(\sigma_g N_g + \sigma_{exc} N_{exc})L] \quad (3)$$

In the particular case of optical absorption saturation, in correspondence of T_{sat} eq(3) becomes:

$$T_{sat} = \exp[-(\sigma_g + \sigma_{exc})N_g L] \quad (4)$$

Eq(4) retains its validity if no light-induced degradation of the molecular absorber takes place in NLO regime, if S_1 is populated and then fully converted into T_1 state with an ISC yield of 100 % (Figure 7). From eq(4) it is found $\sigma_{exc} = 2.9 \times 10^{-16}$ and $1.3 \times 10^{-16} \text{ cm}^2$ at 532 nm for **1** and **4a**, respectively, being $\sigma_g = 2.6 \times 10^{-17} \text{ cm}^2$ for **1** and $\sigma_g = 2.2 \times 10^{-17} \text{ cm}^2$ for **4a** at 532 nm. Eq(4) shows that T_{sat} is a critical transmission value, which is mainly determined by the absorptive properties of the molecular species in the excited state through the property σ_{exc} . On the other hand, ground state absorption is also necessary to start such a NLO phenomenon which is based on sequential multiphoton absorption. Different to eq(1), the formulation of eq(4) takes into account also the occurrence of ground state absorption through the inclusion of the parameter σ_g .

In the case of $(\text{EHO})_8\text{PcIn}(\text{OCOFC}_3)$ (**4a**) the kinetics of NLO absorption decays at different wavelengths were determined (Figure 8). Within the wavelength range 450-520 nm the NLO absorption time profile of **4a** is characterized by an instantaneous peak which decays within the first 2 μs after the initial absorption of the excitation laser shot. Such a finding implies that the excited state which is responsible for the initial variation of absorption has a lifetime not shorter than about 1 μs . Such an excited state should correspond to the excited triplet state T_1 (Figure 7), as previously verified with analogous systems.^{10b,10c,11c} Similar to $(\text{EHO})_8\text{PcIn}(\text{OCOFC}_3)$ (**4a**) in

the short range, i.e. less than 100 ns, $(\text{EHO})_6\text{PhPcInCl}$ (**5**) shows an analogous decay of NLO transmittance at 532 nm when pumped at 560 nm with 5 ns laser pulses (Figure 9). The findings of Figure 9 imply that the lifetime of the absorbing excited state T_1 (Figure 7) is longer than 400 ns for **5**. Moreover, the ISC time for the formation of the absorbing state T_1 results to be less than few ns for $(\text{EHO})_6\text{PhPcInCl}$ (**5**) from the temporal profile of Figure 9.^{10b}

The analysis of the decay profiles in Figure 8 reveals the existence of a slower and less intense component of the NLO absorption variation within the approximate time range 1.5-5 μs .²⁴ The attribution of this second slow absorption component of **4a** is not fully clear at the moment and cannot be directly explained with the four-level model of Figure 7. Cumulative effects generating long-living absorbing excited states or newly formed chemical species in the adopted conditions cannot be excluded as possible origins of such a delayed photophysical phenomenon. Under the conditions of the pump and probe experiments the samples can undergo a process of photochemical degradation. This was verified with $(\text{EHO})_8\text{PcIn}(\text{OCOFC}_3)$ (**4a**), which displayed a decrease of linear absorption (Figure 10) after a series of pump and probe experiments.

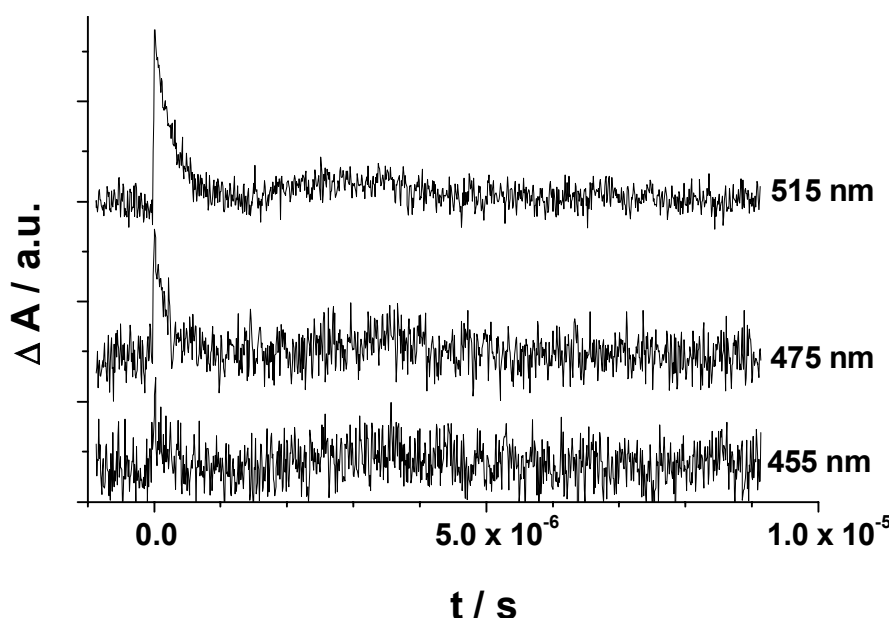


Figure 8. Temporal variations of the NLO absorption change ΔA of $(\text{EHO})_8\text{PcIn}(\text{OCOFC}_3)$ (**4a**) at different wavelengths. The sample **4a** was excited with a series of 250 laser shots at 532 nm with $F_{\text{in}} = 0.25 \text{ J cm}^{-2}$. The frequency of irradiation was 6 Hz. At 532 nm the sample had $T_0 = 0.85$. The reported profile is obtained as the accumulation of 250 consecutive signals. Time $t = 0$ corresponds to the time at which the excitation shot reaches its maximum fluence (temporal gaussian profile).

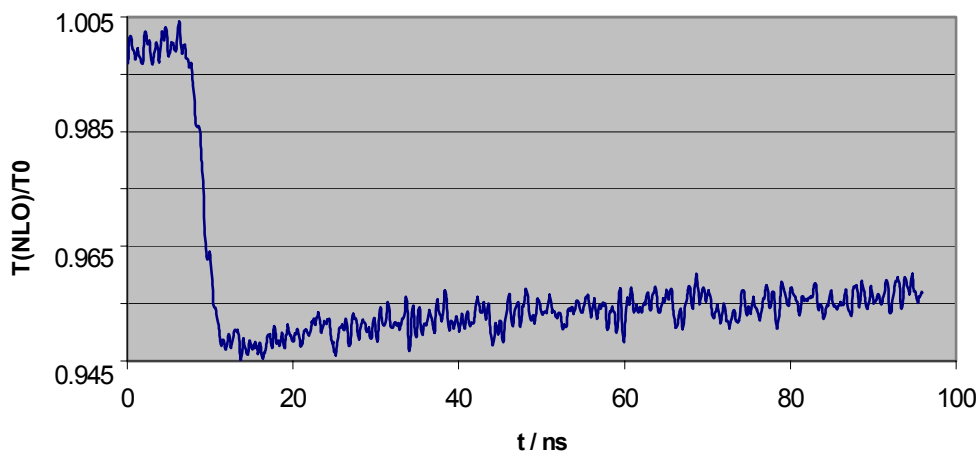


Figure 9. Temporal variations of the ratio of the NLO transmittance T_{NLO} to the linear transmittance T_0 at 532 nm of $(\text{EHO})_6\text{PhPcInCl}$ (**5**). The wavelength of the pump beam was at 563 nm with fluence 0.15 J cm^{-2} . Time $t = 0$ corresponds to the time at which the excitation pulse starts (temporal gaussian profile).

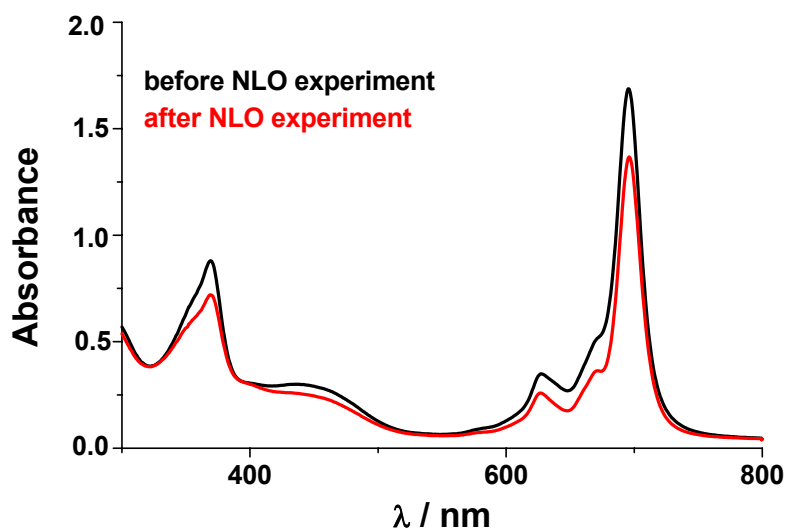
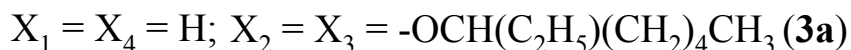
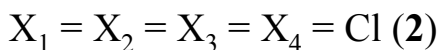
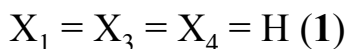
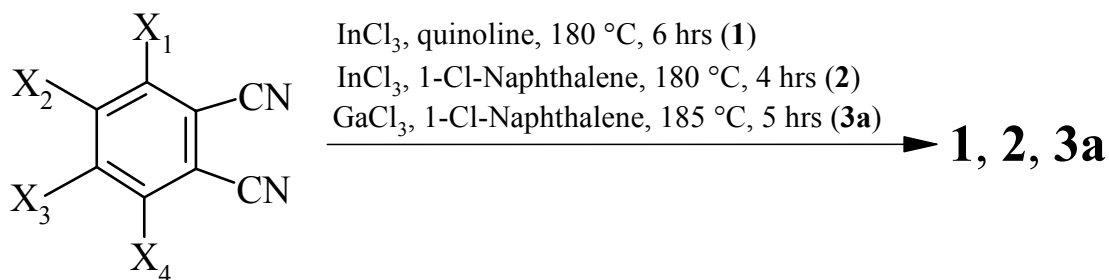


Figure 10. Optical spectrum of $(\text{EHO})_8\text{PcIn}(\text{OCOCF}_3)$ (**4a**) before and after the pump and probe experiment in Figure 8.

Experimental Section

2(3)-Tetratertbutylphthalocyaninato indium chloride (1). $t\text{Bu}_4\text{PcInCl}$ (**1**)²⁵ was prepared from the reaction between InCl_3 (1.5 g, 7 mmol), and 4-*tert*-butylphthalodinitrile^{25b} (5.0 g, 27.5 mmol) in dry quinoline (10 mL) at 180 °C for six hours (Scheme 1). Quinoline was removed from the

reaction mixture by distillation under reduced pressure. After distillation the green residue was chromatographed on silica with CHCl_3 as eluent. The crude compound was finally recrystallized from CH_3OH . Formation yield of **1** (blue-green powder): 49 % (3 g). Elemental analysis [found (theoretical)]: C = 65.2 % (65 %); H = 5.4 % (5.4 %); Cl = 4.1 % (4.0 %); N = 12.3 % (12.6 %). Mass spectrometry data (FD): 886.2 [single positively charged molecular peak, M^+]. $^1\text{H-NMR}$ (CDCl_3): δ = 1.83 [m, 36 H, $\text{C}(\text{CH}_3)_3$], 8.30 (m, 4H, 1-H), 9.30 (m, 4H, 2-H), 9.45 (m, 4H, 2'-H). $^{13}\text{C-NMR}$ (CDCl_3): 32.02 (CH_3), 36.16 [$\text{C}(\text{CH}_3)_3$], 119.75 (C-2'), 123,15 (C-2), 128.52 (C-1), 135.15 (C-3), 137.6 (C-3'), 153.15 (C-4,4'), 154.62 (C-1'). UV/vis absorption peaks (in nm; solvent : CHCl_3): 697 (λ_{max}), 667 (sh), 628, 360, 340 (sh).



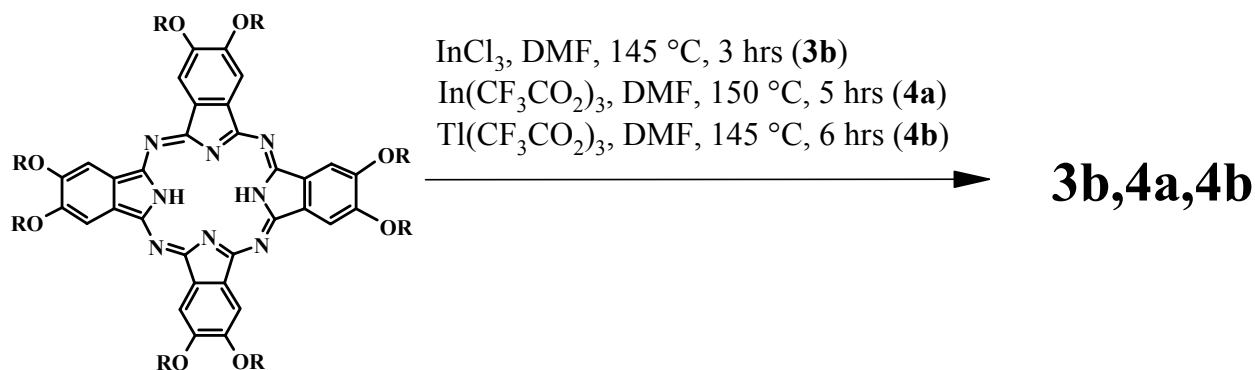
Scheme 1

Hexadecachlorophthalocyaninato indium chloride (2). $\text{Cl}_{16}\text{PcInCl}$ (**2**) was prepared from the template reaction between InCl_3 (0.1 g, 0.5 mmol), and tetrachlorophthalonitrile (0.5 g, 1.9 mmol) in 1-chloronaphthalene (0.2 mL) at 180 °C for four hours (Scheme 1). The reaction mixture was washed several times with CH_3OH and then filtered. After filtration the mixture was dried under vacuum at 230 °C for twenty hours in order to remove the contaminants which were insoluble in CH_3OH . $^{13}\text{C-CP/ MAS-NMR}$ (10^3 Hz): broad peaks at 145 and 116 ppm have been detected. Mass spectrometry (MALDI-TOF): 1215 [molecular peak with the addition of one proton]. Formation yield of **2** (bright green powder): 43 % (0.26 g). UV/vis absorption peaks (in nm; solvent: 1-chloronaphthalene): 744 (b), 697 (λ_{max}), 665 (sh), 630 (b), 425(b), 366 (b).

2,3-Octa-(2-ethyl-hexyloxy)phthalocyaninato gallium chloride (3a). $(\text{EHO})_8\text{PcGaCl}$ (**3a**) was prepared by template reaction of 4,5 bis (2-ethylhexyloxy)-1,2-phthalodinitrile (1.54 g, 4 mmol) with GaCl_3 (260 mg, 1.48 mmol) in 1-chloronaphthalene (4 mL) for five hours at 185 °C (Scheme 1). After cooling down, the crude mixture was poured into 200 ml methanol, stirred for 15 minutes and cooled in the refrigerator for a few hours. After centrifugation, washing with

more methanol and drying, **3a** was three times reprecipitated from hot methanol and dried in vacuum at 100°C. Formation yield of **3a** (dark green powder): 33 % (0.550 g). Elemental analysis [found (theoretical)]: C= 70.09 % (70.16%); H = 8.84 % (8.83 %); N = 6.90 % (6.82%). Mass spectrometry data (FD): 1642.0 [M⁺]. ¹H NMR (THF-d₈): δ = 0.92 (s, br, 48 H, CH₃), 1.33, 1.53 (br, 64 H, CH₂), 2.05 (br, 8 H, CH), 4.24, 4.39 (br, 16 H, OCH₂), 9.16 (br, 8 H, H-2). ¹³C NMR (CDCl₃): 11.1, 14.2 (C-CH₃), 23.0, 23.2, 29.0, 30.8 (C-CH₂), 39.3, 39.8 (C-CH), 72.0 (C-OCH₂), 105.6, 106.2 (br, C-2), 131.4 (br, C-3), 143.5-149.7 (C-4), 153.0 (br, C-1). UV/Vis absorption peaks (in nm; solvent : CH₂Cl₂): 694.5 (λ_{max}), 625.0, 441.0, 357.5.

2,3-Octa-(2-ethyl-hexyloxy)phthalocyaninato indium chloride (3b). (EHO)₈PcInCl (**3b**) was prepared upon reaction of 100 mg InCl₃ (0.45 mmol) with 140 mg octa(2-ethylhexyloxy)PcH₂²⁶ (0.090 mmol) in 20 mL of freshly distilled DMF and 5 mL of anhydrous THF. The reaction mixture was stirred and kept at 145 °C for three hours (Scheme 2). After cooling, the product was precipitated by dropwise addition of water, filtered, and finally washed thoroughly with aqueous CH₃OH. **3b** was obtained after drying in vacuum at 90 °C. Formation yield of **3b** (dark green powder): 88 % (0.13 g). Elemental analysis [found (theoretical)]: C = 67.95 % (68.19%); H = 8.50 % (8.55 %); N = 6.58 % (6.64 %). Mass spectrometry data (FD): 1686.1 [M⁺]. ¹H NMR (THF-d₈): δ = 0.96 (s, br, 48 H, CH₃), 1.42, 1.63 (br, 64 H, CH₂), 1.97 (br, 8 H, CH), 4.36 (br, 16 H, OCH₂), 8.94 (br, 8 H, H-2). ¹³C NMR (CDCl₃): 11.4, 14.1 (C-CH₃), 23.1, 24.1, 29.2, 30.8 (C-CH₂), 39.7 (C-CH), 72.2 (C-OCH₂), 103.7, 105.4, 106.1 (br, C-2), 127.4, 129.8, 131 (br, C-3), 149.7, 150.3, 152.8 (C-4), 154.2, 157.1 (br, C-1). UV/Vis absorption peaks (in nm; solvent: CH₂Cl₂): 699 (λ_{max}), 671.5, 629.5, 446, 401, 363.



Scheme 2

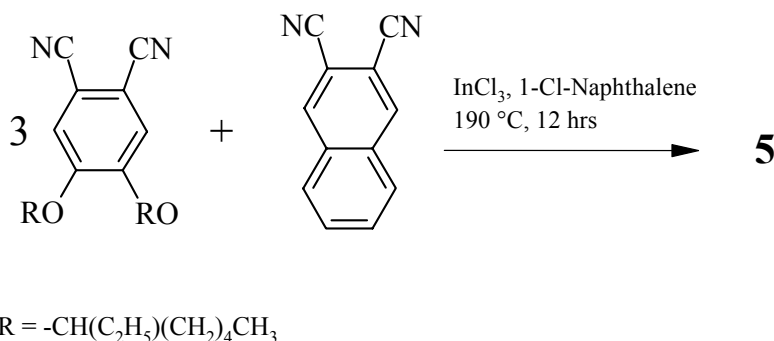
2,3-Octa-(2-ethyl-hexyloxy)phthalocyaninato indium trifluoroacetate (4a). (EHO)₈PcIn(CO₂CF₃) (**4a**) was prepared upon reaction of In(CF₃COO)₃ (200 mg, 0.4 mmol) and octa(2-ethylhexyloxy)PcH₂²⁶ (250 mg, 0.160 mmol) in 20 ml of freshly distilled DMF and 5 ml of quinoline (Scheme 2). The reaction mixture was stirred and boiled at 145 °C for five hours. After cooling, the product was precipitated upon dropwise addition of a 10% solution of NaOH in CH₃OH. After filtration, the precipitate was washed several times with aqueous CH₃OH and

finally dried in vacuum at 70°C. Formation yield of **4a** (dark green powder): 73 % (200 mg). Mass spectrometry data (FD): 1710.2 [M⁺]. ¹H NMR (THF-d₈): δ = 1.10 (s, br, 24 H, CH₃), 1.22 (s, br, 24 H, CH₃) 1.30, 1.45 (br, 64 H, CH₂), 2.22 (br, 8 H, CH), 4.54 (br, 16 H, OCH₂), 9.15 (br, 8 H, H-2). ¹³C NMR (THF-d₈): 12.2, 12.5, 15.2 (C-CH₃), 24.9, 25.8, 30.9, 33.2 (C-CH₂), 41.4, 41.6 (C-CH), 73.3 (C-OCH₂), 107.4 (br, C-2), 135.7 (br, C-3), 144.1-148.3 (C-4), 151.0-154.3 (br, C-1), 157.4(C=O). IR (KBr): ν (cm⁻¹): 2960, 2932, 2849, 1702 (C=O), 1601, 1370, 1269, 1200. 1042, 878, 842, 745 (C-F), 716 (C-F), 666. UV/Vis absorption peaks (in nm, solvent: CH₂Cl₂): 723.5 (λ_{max}), 645.5, 402.

2,3-Octa-(2-ethyl-hexyloxy)phthalocyaninato thallium trifluoroacetate (4b). (EHO)₈PcTl(CO₂CF₃) (**4b**) was prepared upon reaction of 120 mg Tl(CF₃COO)₃ (0.2 mmol) with 125 mg octa(2-ethylhexyloxy)PcH₂ (0.080 mmol)²⁶ in 15 mL of freshly distilled DMF and 4 mL of quinoline (Scheme 2). The reaction mixture was stirred and kept at 145 °C for six hours. After cooling, the product was precipitated upon a dropwise addition of a 10% solution of NaOH in CH₃OH, filtered, washed through several times with aqueous methanol and dried in vacuum at 70°C. Formation yield of **4b** (dark green powder): 60 % (100 mg). Elemental analysis [found (theoretical)]: C = 61.96 % (62.93 %); H = 5.65 % (6.82 %); N = 5.97 % (6.04 %). Mass spectrometry data (FD): 1855.6 [M⁺]. ¹H NMR (THF-d₈): δ = 1.00 (s, br, 24 H, CH₃), 1.12 (s, br, 24 H, CH₃) 1.33, 1.49 (br, 64 H, CH₂), 1.98 (br, 8 H, CH), 4.48 (br, 16 H, OCH₂), 8.95 (br, 8 H, H-2). ¹³C NMR (THF-d₈): 12.2, 12.5, 15.0, 15.2 (C-CH₃), 24.7, 25.8, 30.7, 30.9, 32.2, 33.2 (C-CH₂), 41.4, 41.7 (C-CH), 73.0 (C-OCH₂), 107.0 (br, C-2), 135.2 (br, C-3), 143.5-149.7 (C-4), 151.3-153.8(br, C-1), 157.1 (C=O). UV/Vis absorption peaks (in nm, solvent : CH₂Cl₂): 720.5 (λ_{max}), 647.5, 403.5, 364.5.

2,3,9,10,16,17-hexa-(2-ethyl-hexyloxy)monobenzophthalocyaninato indium chloride (5). (EHO)₆PhPcInCl (**5**) was prepared by stastical condensation of 4,5 bis-(2-ethylhexyloxy)-1,2-phthalodinitrile (1.27 g, 3.3 mmol) and 2,3-naphthalodinitrile (180 mg, 1 mmol), with InCl₃ (220 mg, 1 mmol) in 1-chloronaphthalene (5 ml) at 190° C for 12 hours (Scheme 3). After cooling, the crude mixture was poured into 200 ml CH₃OH, stirred for 15 minutes and kept in the refrigerator for four hours. After centrifugation of the cooled solution the solvent CH₃OH was removed and the reaction mixture was washed with CH₃OH for the second time and finally dried. Successively the dried mixture underwent a separation process through column chromatography on SiO₂ using CH₂Cl₂ as eluent. (EHO)₈PcInCl (**3b**) constituted the first fraction. After removal of **3b** the eluent was changed and the mixture CH₂Cl₂/THF in the volume ratio 25:1 was used, instead, in order to obtain **5** in the second fraction. The successive fractions were discarded. After evaporation of the solvent, **3b** and **5** were washed in hot CH₃OH for three times and dried in vacuum at 100°C. Formation yield of **5** (dark green powder): 27 % (400 mg). Elemental analysis [found (theoretical)]: C = 69.3 % (67.89 %); H = 8.8 % (8.00 %); N = 7.8 % (7.54 %). Mass spectrometry data (field desorption operation mode): 1481.6 [M⁺], 1378.2 [M⁺-C₈H₁₇]. ¹H NMR (THF-d₈): δ = 1.00 (s, br, 18 H, CH₃), 1.10 (s, br, 18 H, CH₃) 1.31, 1.52 (br, 48 H, CH₂), 1.98 (br, 6 H, CH), 4.48 (br, 12 H, OCH₂), 7.62 (s, 2 H, H-6), 8.31 (s, br, 2 H, H-5), 8.75 (br, 6 H, H-9). 9.95 (br, 2 H, H-3). ¹³C NMR (THF-d₈): 12.2, 12.6, 14.2 (C-CH₃), 24.5,

25.9, 30.7, 30.9, 32.6, 33.4 (C-CH₂), 41.4, 41.8 (C-CH), 73.2 (C-OCH₂), 107.0 (br, C-9), 120.0 (br, C-3), 130.0-132.1 (br, C-4, C-5, C-6), 135.2, 135.4 (br, C-2, C-8), 143.5-149.7 (C-1, C-7), 151.3-153.8 (br, C-10). UV/vis absorption peaks (in nm; solvent: toluene): 685 (λ_{\max}), 655(sh), 622, 440 (b), 360.



Scheme 3

Optical transmission measurement. For the determination of NLO transmission of the complexes here presented we used the second harmonics of emission of a pulsed Nd:YAG laser at 532 nm as light source. The incident beam had temporal and spatial gaussian profiles, and the pulse duration was in the range 5-10 ns. NLO transmission curves have been taken with $f/\text{number} = 65$ using a Gaussian beam as input beam when the sample is located in correspondence of the beam focus. The choice of such “slow” optics of incidence was dictated by the need of minimizing unavoidable heating effects during the positioning of the sample in correspondence of the focal plane. Beam waist is about 40 μm in the experiments of NLO transmission determination. The collection of the transmitted beam was done in the open aperture configuration using the same optics as for the incident beam.

Time stability of the samples (liquid solutions) for NLO experiments has been checked adopting the following three procedures: 1) daily check of the linear optical spectrum of the sample for one week; 2) comparison of the NLO transmission data obtained at 10 Hz of repetition rate and with single pulse irradiation; 3) irradiation of the sample solution with fixed energy pulses at 10 Hz of repetition rate for thirty minutes and successive check of the NLO transmission. Possible solvent effects on the NLO transmission of the samples were studied by measuring the JNLO transmission of the pure solvent. Solvents for NLO experiments were used without further purification (commercial spectroscopic grade). Calibration of the optical apparatus was conducted using reference samples of C₆₀ as standard. The NLO properties of the different samples were characterized in the same conditions of irradiation and compared with those of the standard.

Acknowledgements

We thank Dr. Kenneth McEwan [DSTL, Malvern(UK)] for having provided some data. Financial support from EU (Grant No. HPRN-CT-2002-00323) is gratefully acknowledged.

References and Footnotes

1. (a) Leznoff, C.C.; Lever, A.B.P. (Eds.) *Phthalocyanines: Properties and Applications*; VCH: Weinheim, 1989-1996; *Voll. 1-4*. (b) Kadish, K.M.; Smith, K.M.; Guillard, R. (Eds.) *Porphyrin Handbook*; Elsevier Science: San Diego, 2003; *Voll. 11-20*.
2. (a) Eastwood, D.; Edwards, L.; Gouterman, M.; Steinfeld, J.I. *J. Mol. Spectr.* **1966**, *20*, 381. (b) Mack, J.; Stillman, M.J In *Porphyrin Handbook*; Kadish, K.M.; Smith, K.M.; Guillard, R. Eds.; Elsevier, 2003; Vol. 16, p 43.
3. (a) Eley, D.D. *Nature* **1948**, *162*, 819; (b) Hanack, M.; Lang, M. *Adv. Mat.* **1994**, *6*, 819.
4. (a) Popovic, Z.D.; Menzel, E.R. *J. Chem. Phys.* **1979**, *71*, 5090. (b) Loutfy, R. O.; Hor, A.M.; Hsiao, C.K.; Baranyi, G.; Kazmaier, P. *Pure Appl. Chem.* **1988**, *60*, 1047. (c) Law, K.Y. *Chem. Rev.* **1993**, *93*, 449. (d) Umeda, M.; Mohamedi, M.; Itoh, T.; Uchida, I. *J. Appl. Phys.* **2001**, *90*, 3984.
5. (a) De la Torre, G.; Vazquez, P.; Agullo-Lopez, F.; Torres, T. *Chem. Rev.* **2004**, *104*, 3723. (b) Coe, B.J. In *Comprehensive Coordination Chemistry II*; McCleverty, J.A.; Meyer, T.J. Eds.; Elsevier, 2004; Vol. 2, p 621.
6. (a) Moser, F.H. In : *Pigment Handbook*; Patton, T.C. Ed.; Wiley, 1973; *Vol. 1*, p 679 and p 689. (b) Erk, P.; Hengelsberg, H. In *Porphyrin Handbook*; Kadish, K.M.; Smith, K.M.; Guillard, R. Eds.; Elsevier, 2003; *Vol. 19*, p 105.
7. (a) Collins, R. A.; Mohammed, K. A. *J. Phys. D: Appl. Phys.* **1988**, *21*, 154. (b) Wright, J.D. *Progr. Surf. Sci.* **1989**, *31*, 1. (c) Temofonte, T.A.; Schoch, K.F. *J. Appl. Phys.* **1989**, *65*, 1350. (d) Zhou, R.; Josse, F.; Gopel, W.; Oeztuerk, Z. Z.; Bekaroglu, O. *Appl. Organometal. Chem.* **1996**, *10*, 557. (e) Guillaud, G.; Simon, J.; Germain, J.P. *Coord. Chem. Rev.* **1998**, *178-180*, 1433.
8. (a) Dini, D.; Barthel, M.; Hanack, M. *Eur. J. Org. Chem.* 2001, 3759. (b) Hanack, M.; Dini, D.; Barthel, M.; Vagin, S. *Chem. Rec.* **2002**, *2*, 129. (c) O'Flaherty, S.M.; Hold, S.V.; Cook, M.J.; Torres, T.; Chen, Y.; Hanack, M.; Blau, W.J. *Adv. Mat.* **2003**, *15*, 19. (d) Calvete, M.; Yang, G.Y.; Hanack, M. *Synth. Met.* **2004**, *141*, 231.
9. For the use of Pcs in photodynamic therapy see for example: (a) Rosenthal, I. *Photochem. Photobiol.* **1991**, *53*, 859. (b) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19. (c) Allen, C.M.; Sharman, W.M.; Van Lier, J.E. *J. Porphyrins Phthalocyanines* **2001**, *5*, 161. For the use of Pcs in electrochromic devices see for example: (d) Nicholson, M.M. In: *Phthalocyanines: Properties and Applications*; Cliznoff, C.C.; Lever, A.B.P. Eds.; VCH, 1993; *Vol. 3*, p 71. For the use of Pcs in digital recording applications see for example: (e) Hurditch, R. *Adv.*

- Colour Sci. Techn.* **2001**, *4*, 33. For the use of Pcs in photovoltaics see for example: (f) Wohrle, D.; Kreienhoop, L.; Schlettwein, D. *Phthalocyanines* **1996**, *4*, 219. For the use of Pcs in electrocatalysis see for example: (e) Vasudevan, P.; Phougat, N.; Shukla, A.K. *Appl. Organomet. Chem.* **1996**, *10*, 591. (f) Zagal, J.H. *Coord. Chem. Rev.* **1992**, *119*, 89.
10. (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) Shirk J.S.; Pong, R.G.S.; Flom S.R.; Heckmann H.; Hanack M. *J. Phys. Chem. A* **2000**, *104*, 1438.
 11. (a) Perry, J.W. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H.S.; Miyata S. Eds.; CRC Press, 1997, p 813; (b) Sun, Y.P.; Riggs, J.E. *Int. Rev. Phys.Chem.* **1999**, *18*, 43; (c) Chen, Y.; Dini, D.; Hanack, M.; Fujitsuka, M.; Ito, O. *Chem. Comm.* **2004**, 340.
 12. Huffman, P.D.; Fitzgerald, J.P.; Shirk, J.S. Abstr. 223rd ACS Natl. Meet., Orlando (USA), April 7-11, 2002 CHED-530.
 13. Lower, S.K.; El-Sayed, M.A. *Chem. Rev.* **1966**, *66*, 199.
 14. (a) Hanack, M.; Heckmann, H.; Polley R. In : *Methoden der Organischen Chemie (Houben–Weyl)*, 4th Ed.; Thieme Verlag, 1997, *Vol. E9d*; p 717. (b) McKeown, N.B. In *Science of Synthesis(Houben–Weyl Methods of Molecular Transformations)*; Thieme Verlag, 2004, *Vol.17*; p 1237.
 15. Snow, A.R. In : *Porphyrin Handbook*; Kadish, K.M.; Smith, K.M.; Guillard, R. Eds.; Elsevier, 2003; *Vol. 17*, p 129.
 16. Kernag, C.A.; McGrath, D.V. Abstr. 223rd ACS Natl. Meet. Orlando (USA), April 7-11, 2002 ORGN-315; (b) Flom, S.R. Pong, R.G.S.; Shirk, J.S.; Bartoli, F.J.; Boyle, M.E.; Snow, A.W. Abstr. 212th ACS Natl. Meet. Orlando (USA), August 25-29, 1996 PHYS-277.
 17. (a) Giuliano, C.R.; Hess, L.D. *J. Quantum Electron.* **1967**, *3*, 358. (b) Harter, D.J.; Shand, M.L.; Band, Y.B. *J. Appl. Phys.* **1984**, *56*, 865.
 18. Hercher, M. *Appl. Opt.* **1967**, *9*, 947.
 19. Blau, W.; Byrne, H.; Dennis, W.M.; Kelly, J.M. *Opt. Comm.* **1985**, *56*, 25.
 20. Nalwa, H.S.; Shirk, J.S. In *Phthalocyanines: Properties and Applications*; Cliznoff, C.C.; Lever, A.B.P. Eds.; VCH, 1996; *Vol. 4*, p 79.
 21. Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, 1991; pp 121-130.
 22. Calvete, M.J.F.; Dini, D.; Flom, S.R.; Hanack, M.; Pong, R.G.S.; Shirk, J.S. *Eur. J. Org. Chem.* **2005**, 3499.
 23. (a) Vagin, S.; Barthel, M.; Dini, D.; Hanack, M. *Inorg. Chem.* **2003**, *42*, 2683. (b) Tutt, L.W.; Boggess, T.F. *Prog. Quant. Electron.* **1993**, *17*, 299.
 24. Hanack, M.; Schneider, T.; Barthel, M.; Shirk, J.S.; Flom, S.R.; Pong, R.G.S. *Coord. Chem. Rev.* **2001**, *219-221*, 235.
 25. (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.

26. Calvete, M. Ph.D. thesis, University of Tübingen (Germany), 2004.