

Second-Harmonic Generation from Axially Substituted Indium Phthalocyanines

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The quadratic hyperpolarizabilities of three axially substituted Indium phthalocyanines (In-Pcs) (**1**–**3**) in chloroform solution have been measured by the EFISH technique at $\lambda = 1064$ nm. A maximum value of 37.4×10^{-30} esu has been obtained for the trifluoromethylphenyl-substituted compound **3**. The data have been analyzed with a two-level model corresponding to the Q-band and so the nonresonant values for the quadratic hyperpolarizability, $\beta_z(0)$, have been determined by taking into account the electronic contribution to γ_{EFISH} . The three components $\chi_{15}^{(2)}$, $\chi_{31}^{(2)}$, and $\chi_{33}^{(2)}$ of the susceptibility tensor have also been obtained for spin-coated films containing the three compounds dissolved in PMMA. Susceptibilities reach the highest values, $\chi_{15}^{(2)} = 3.3 \times 10^{-10}$ esu, $\chi_{31}^{(2)} = 3.9 \times 10^{-10}$ esu, and $\chi_{33}^{(2)} = 13.1 \times 10^{-10}$ esu, for compound **3**. Kleinman symmetry is approximately obeyed particularly for the Cl-substituted compound **1**.

1. Introduction

Phthalocyanines (Pcs)¹ are highly conjugated planar molecules with an extensive delocalized π -electron system that exhibits interesting perspectives for nonlinear optical (NLO) applications.^{2–6} On one side, high cubic hyperpolarizabilities as well as good optical limiting capabilities have been reported. On the other hand, synthetic strategies are being developed to prepare noncentrosymmetric Pc derivatives with potential interest for second-harmonic generation (SHG) and electrooptic modulation. Two main approaches have been so far used,^{5,6} (a) push–pull peripheral substitution of Pcs with strong donor and acceptor groups, (b) axial substitution on the central metal and (c) synthesis of intrinsically unsymmetric Pc-related compounds. Peripheral substitution has been successfully tried although susceptibility values are not remarkable.^{7–12} On the other hand, strategies b and c appear quite promising. With regard to strategy b, information is still scarce although relatively large SHG responses have been achieved through axial substitution.^{13,14} On the other hand, intrinsically unsymmetric Pc derivatives, such as triazophthalocyanines¹⁵ and subphthalocyanines (SubPcs)^{16,17} have yielded high susceptibility values in both solutions and spin-coated films, standing out the potential of strategy c. SubPcs deserve special mention since they constitute a particularly relevant example that combines both strategies b and c and offer a good reference for comparative studies. They are pyramid-shaped molecules with C_{3v} symmetry consisting of three coupled isoindole units with a boron atom in the center linked to an axial substituent. A strong aromatic character is promoted by their extended system of 14 delocalized π -electrons.

To further explore the interest of strategy b, several indium–phthalocyanines (In-Pcs) axially substituted either by a chloro

atom (**1**) or by a phenyl (**2**) or trifluoromethylphenyl group (**3**) have been investigated. The chemical structure of the molecules studied in this work is depicted in Figure 1. The compounds had been previously described by us.¹⁸ The axial group R induces asymmetry and provides the molecule with an axial electric dipole moment, i.e., perpendicular to the macrocycle plane. In-Pcs have already been satisfactorily applied to optical limiting devices due to the favorable structure of electronic levels and the high singlet–triplet transfer rate.^{19–22} However, their harmonic-generation capabilities, which rely on different physical mechanisms and obey different performance criteria, have not been investigated as far as we know. The purpose of this work has been to evaluate the potential of these molecules for second-order nonlinear optics. To that end, SHG experiments have been performed on solution and on spin-coated films. One specific aim of this work is to compare their SHG performance with that of other unsymmetric Pc derivatives, particularly SubPcs (Figure 2), and so elucidate the role of molecular geometry and symmetry on the NLO response. In particular, the basic point symmetry of our In-Pcs molecules is C_{4v} instead of the C_{3v} of the hexasubstituted SubPcs previously studied by us.¹⁷ This should influence the ratio between the diagonal and off-diagonal components of the hyperpolarizability tensor, and so the dipolar/octupolar character²³ of the SHG.

2. Experimental Section

2.1. Dipole Moments. Dipole moments have been measured by the classical Guggenheim method.²⁴

2.2. EFISH Experiments. EFISH experiments²⁵ have been performed in chloroform solutions at the 1064 nm fundamental wavelength obtained from a Q-switched Nd³⁺: yttrium–

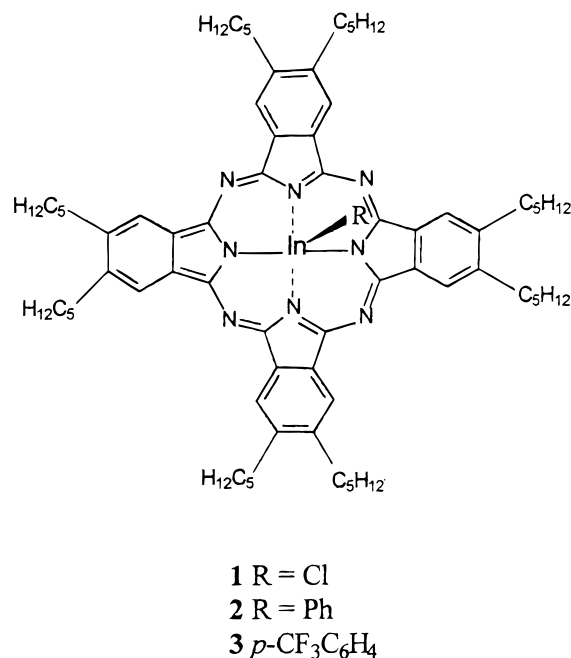


Figure 1. Chemical structure of indium-phthalocyanines 1–3.

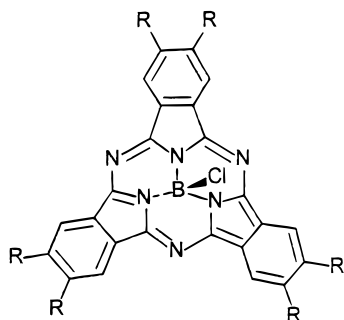


Figure 2. Chemical structure of a hexasubstituted subphthalocyanine.

aluminum-garnet (YAG) laser, with a 10 ns pulse duration and a repetition rate of 10 Hz. A liquid cell with thick windows in the wedge configuration²⁶ was used to obtain a Maker fringes pattern. The incident beam was synchronized with a dc field applied to the solution in order to break its centrosymmetry.

2.3. Film Preparation. Films were prepared by spin-coating from a chlorobenzene solution of approximately 7 wt % of the corresponding InPc in PMMA. This solution was previously filtered to remove impurity particles and then spun at 3000–5000 rpm onto microscope glass slides. A baking processes at 100 °C during 15 h was carried out to remove the solvent as completely as possible. The thickness of the films, measured by a standard profilometer, was found to be around 2 μm. The concentrations of the InPcs in the film were determined by comparing their optical absorption spectra in spin-coated films with those measured in chloroform solution at known concentrations. The obtained values are included in Table 1.

2.4. Corona Poling. To induce molecular ordering in the spin-coated films, and so break their centrosymmetry a corona poling technique was used.²⁷ A needle, at a static potential of 9000 V, was positioned at ~1 cm above the grounded sample. The temperature during poling was ca. 80 °C, and the poling time was 2 h. Under these conditions a steady-state corresponding to thermodynamical equilibrium in the presence of the field appears to be achieved.

2.5. SHG Experiments. The experimental setup and the film geometry are shown in Figure 3. The SHG intensity was

TABLE 1: Components of the Susceptibility Tensor, Molecular Concentrations, and Thickness of the Spin-Coated Films Containing Compounds 1–3^a

	thickness (μm)	10 ⁻¹⁹ <i>N</i> (cm ⁻³)	10 ¹⁰ χ ₁₅ ⁽²⁾ (esu)	10 ¹⁰ χ ₃₁ ⁽²⁾ (esu)	10 ¹⁰ χ ₃₃ ⁽²⁾ (esu)
1	2.0 ± 0.1	0.5	1.9	2.0	5
2	1.9 ± 0.1	2.8	2.3	2.8	10
3	2.0 ± 0.1	1.3	3.3	3.9	13

^a The experimental error is around 6% for χ₁₅⁽²⁾ and 20% for χ₃₁⁽²⁾.

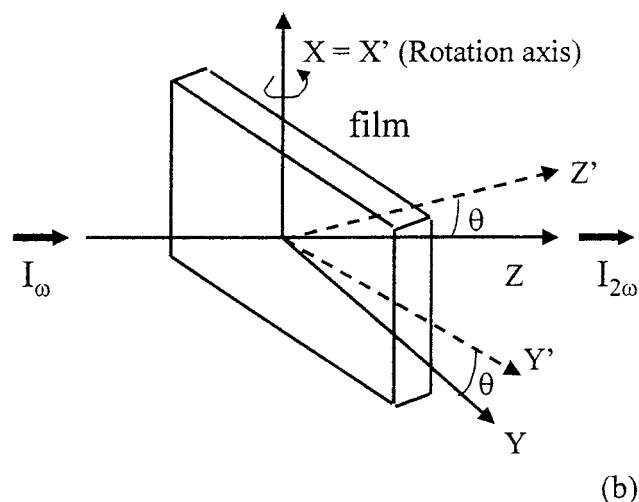
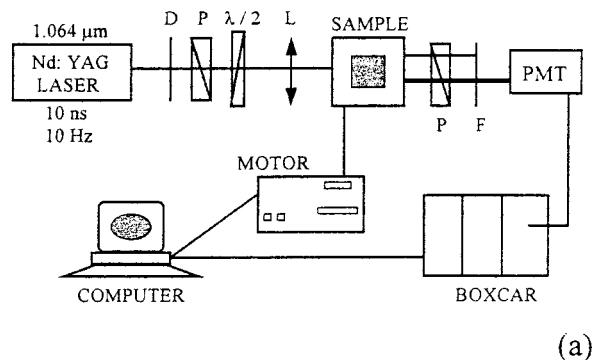


Figure 3. (a) Experimental setup. (b) Film geometry.

detected as a function of the incidence angle of the laser beam, which is changed by rotating the sample with regard to an axis (X) in the film plane and perpendicular to the incident fundamental beam (along the Z axis).

The same laser source as in EFISH experiments was used as fundamental light. A linear polarizer and a half-wave plate are placed in front of the sample, to obtain the three polarizations of the incident beam needed to determine the three independent components of the χ_{ij}⁽²⁾ tensor under the C_{∞v} symmetry of the poled spin-coated films.^{28,29} Those polarizations are configuration i along the X axis, configuration ii along the Y axis, and configuration iii at 45° from either the X or Y axis. We also used a polarizer behind the sample to measure only one polarization component of the second-harmonic signal (see below). This signal is detected by a photomultiplier tube, averaged by a boxcar integrator, and stored in a computer.

Experiments with the same geometry, using an X-polarized incident beam and detecting also X-polarized second-harmonic signal were performed on a X-cut congruent LiNbO₃ plate to be used as a reference. (The X-axis is parallel to the *c*-axis of the crystal, so the only component contributing to the SHG intensity is χ₃₃⁽²⁾ = 1.96 × 10⁻⁷ esu³⁰).

TABLE 2: Measured Permanent Dipole Moment and Cubic Hyperpolarizability from the EFISH Experiment^a

	$\mu^{(0)}$ (D)	$10^{33}\gamma_{\text{EFISH}}^{(0)}$ (1064 nm) (esu)	$10^{46}\mu^{(0)}\beta$ (1064 nm) (esu)	$10^{30}\beta$ (1064 nm) (esu)
1	15.6	-2.7	-5.5	-35.5
2	13.8	-3.8	-7.8	-56.5
3	10.7	-2.8	-5.7	-53.7

^a Values of the quadratic hyperpolarizability and the product $\mu^{(0)}\beta_z$ (1064 nm) are obtained by neglecting the electronic contribution to EFISH.

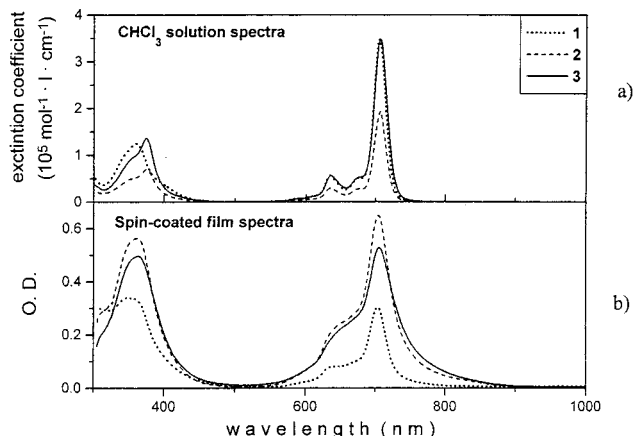


Figure 4. Optical absorption spectra of In-Pcs 1–3 in (a) chloroform solution and (b) spin-coated films. The thickness and the concentration of the spin-coated film are included in Table 1.

3. Results

3.1. Dipole Moments. Measured ground-state dipole moments are listed in Table 2. They are quite comparable to those reported for SubPcs substituted with strong acceptor groups (alkylsulfonyl or nitro)¹⁷ as well as to those measured for substituted triazolephthalocyanines.¹⁵ On the other hand, they are larger than those reported for most peripherally substituted Pcs investigated in a previous work.¹²

3.2. Optical Absorption Data. The absorption spectra of In-Pcs in chloroform solution are illustrated in Figure 4a. The spectra show well-defined Q and B bands with clear features at the short-wavelength side of the narrow Q-band. In accordance with other axial and peripheral substitutions, the peak position of this band is essentially independent of the axial substituent, although some differences appear in the corresponding extinction coefficients. Some spectral changes are observed at the B-band region. On the other hand, the spectra of films (Figure 4b) are essentially similar to those in solution, although they show substantial broadening that smooths out the spectral features around the Q-band. In relation to SHG experiments at 1064 nm, it is interesting to note that both the fundamental and harmonic waves are not appreciably absorbed.

3.3. SHG Results in Solution: Hyperpolarizabilities. The values measured for γ_{EFISH} at $\lambda = 1064$ nm are negative and summarized in Table 2. They include an electronic as well as an orientational contribution in accordance with the expression³¹

$$\gamma_{\text{EFISH}} = \gamma_{\text{elec}} + \gamma_{\text{orient}} = \gamma_{\text{elec}} + \frac{\mu^{(0)}\beta_z}{5kT} \quad (1)$$

where $\mu^{(0)}$ is the permanent dipole moment of the A_1 ground state and β_z is the z component of the dipolar part of the quadratic hyperpolarizability. Following symmetry considerations for the C_{4v} molecular group of the InPcs, it is assumed that the molecular z axis lies parallel to the ground-state dipole moment.

It is, in principle, difficult to separate both electronic and orientational contributions to γ_{EFISH} . One possible approach, that is often used, is to ignore the electronic contribution, i.e., $\gamma_{\text{EFISH}} = \gamma_{\text{orient}}$. Under this assumption the $\mu^{(0)}\beta_z$ value appearing in γ_{orient} has been obtained, and it is listed in Table 2 for the three compounds. The negative values for γ_{EFISH} are then associated with opposite directions for the permanent ground-state dipole vector and the vector part of the hyperpolarizability. Absolute values given in Table 2 are significant. However, for a more detailed assessment the values at zero frequency should be estimated (see next).

A more realistic estimate of the EFISH hyperpolarizability requires some corrections for the electronic contribution to γ_{EFISH} . A simple and approximate way to evaluate this correction is to use a two-level scheme referred to the dominant Q-band. This approach has been satisfactorily used in previous work.^{12,32} Although a two-level model has severe limitations, it should provide a good approximation when the system has a narrow dominant low-energy transition, well separated from higher bands, as exemplified by the Q-band in Pcs. One can, then, calculate both the electronic and the orientational contributions to γ_{EFISH} using the general formulas,^{32,33} i.e., for any symmetry,

$$\gamma_{\text{EFISH}} = -\frac{6\omega_{01}}{5\hbar^3} \frac{[2(\mu_{01}^x)^2 + (\mu_{01}^z)^2]^2}{(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)} + \frac{\Delta\mu_{01}^2 \left[\frac{2}{3}(\mu_{01}^x)^2 + (\mu_{01}^z)^2 \right]^2}{(\omega_{01}^2 - 4\omega^2)^2(\omega_{01}^2 - \omega^2)^2} \frac{3\omega_{01}^3(2\omega_{01}^2 - 5\omega^2)}{5\hbar^3} + \frac{3\omega_{01}^2 \Delta\mu_{01}}{2\hbar^2} \left[\frac{\frac{2}{3}(\mu_{01}^x)^2 + (\mu_{01}^z)^2}{(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)} \right] \quad (2)$$

The three terms in the right-hand side successively correspond to the symmetric electronic, unsymmetrical electronic, and orientational contribution to γ_{EFISH} . ω_{01} is the peak frequency of the Q-band, μ_{01}^x , μ_{01}^y , and μ_{01}^z are the components of the transition dipole moment, and $\Delta\mu_{01}$ is the mesomeric dipole moment (difference between the permanent dipole moments, μ_1 of the excited and μ_0 of the ground state). The Z -axis is along the 4-fold molecular axis. μ_{01} and ω_{01} are obtained from the linear absorption spectra and the only unknown parameter in (2) is $\Delta\mu_{01}$. Fortunately, the C_{4v} symmetry of the InPcs ensures that the permanent dipole moments, μ_0 and μ_1 , of the ground A_{1g} and excited E_u states respectively of the Q-band transition, and so $\Delta\mu_{01} = \mu_1 - \mu_0$ are oriented along the Z -axis. Moreover, the transition moment for the Q-band ($A_{1g} \rightarrow E_u$) may only have X , Y components. Therefore, formula 2 simplifies to

$$\gamma_{\text{EFISH}} = -\frac{6\mu_{01}^4}{5\hbar^3} \frac{\omega_{01}}{(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)} + \frac{\mu_{01}^2 \Delta\mu_{01}^2}{5\hbar^3} \frac{3\omega_{01}^3(2\omega_{01}^2 - 5\omega^2)}{(\omega_{01}^2 - 4\omega^2)^2(\omega_{01}^2 - \omega^2)^2} + \frac{\mu^{(0)}}{5kT} \left[\frac{\mu_{01}^2 \Delta\mu_{01} \omega_{01}^2}{2\hbar^2(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)} \right] \quad (3)$$

Then, from the fitting of eq 3 to the measured γ_{EFISH} , one obtains $\Delta\mu_{01}$ and, thus, both γ_{elec} and γ_{orient} that are included in Table 3. One notes that the electronic component is positive and so the orientational part becomes negative and larger than

TABLE 3: Transition Dipole Moment Associated with the Q-band (μ_{01}), Mesomeric Dipole Moment ($\Delta\mu_{01} = \mu^{(1)} - \mu^{(0)}$) Calculated Using a Two-Level Model, Off-Resonant Dipolar First-Order Hyperpolarizability ($\beta_z(0)$), Product of the Permanent Dipole Moment of the Ground State and Off-Resonant Quadratic Hyperpolarizability ($\mu^{(0)}\beta_z(0)$)^a

	μ_{01} (D)	$\Delta\mu_{01}$ (D)	$10^{33}\gamma_{\text{rot}}(1064)$ nm (esu)	$10^{33}\gamma_{\text{elec}}(1064)$ nm (esu)	$10^{30}\beta_z(0)$ (esu)	$10^{46}\mu^{(0)}\beta_z(0)$ (esu)
1	10.9	3.4	-4.5	1.7	25.0	3.9
2	7.8	7.1	-4.2	0.4	27.0	3.7
3	10.5	5.1	-4.3	1.5	35.3	3.8

^a Electronic (γ_{elec}) and orientational (γ_{orient}) contributions to the second-order hyperpolarizability γ_{EFISH} are also included.

those calculated when γ_{elec} is ignored (see Table 2). Moreover, the nonresonant product $\mu^{(0)}\beta_z(0)$ and consequently $\beta_z(0)$ can, then, be derived from the two-level expression given by

$$\beta_z(0) = \frac{|\mu_{01}|^2 \Delta\mu_{01}}{2\hbar^2} \quad (4)$$

where

$$|\mu_{01}|^2 = (\mu_{01}^x)^2 + (\mu_{01}^y)^2$$

The calculated values are also given in Table 3. It is concluded that the corrected values of $\mu^{(0)}\beta_z$ are about 50% larger than those obtained when the electronic contribution to γ_{EFISH} is neglected, thus illustrating the relevance of taking this contribution into account for a proper analysis of the data. Nonresonant values $\beta_z(0)$ are comparable to those derived for a number of peripherally substituted Pcs,¹² although smaller than those reported for SubPcs.¹⁷ It is remarkable that the values for the electronic and orientational contributions to γ_{EFISH} , and so of the $\mu^{(0)}\beta_z(0)$ product, are essentially independent of the assumed dipolar moment and so are not very sensitive to errors in the measurement of $\mu^{(0)}$.

3.4. SHG Data on Films: Susceptibilities. The $\chi_{il}^{(2)}$ values were determined from the analysis of the Maker fringes following the procedure given in previous references.^{20,21} The formula giving the effective second-harmonic intensity as a function of the rotation angle θ can be expressed as³¹

$$I_{2\omega}(\theta) = \frac{64\pi^3 \omega^2 \chi_{\text{eff}}^2 I_0^2 T}{n_\omega^2 n_{2\omega} c^3} e^{(-\alpha_{2\omega} L / 2 \cos \theta')} \frac{\cosh\left(\frac{\alpha_{2\omega} L}{2 \cos \theta'}\right) - \cos\left(\frac{\Delta k L}{\cos \theta'}\right)}{\frac{\alpha_{2\omega}^2}{4} + \Delta k^2} \quad (5)$$

I_0 being the incident fundamental intensity, L the film thickness, and T an overall transmission factor accounting for both fundamental and harmonic reflections at the various boundaries. The angle θ' is the rotation angle inside the film ($\sin \theta' = (I/n_\omega) \sin \theta$), and $\Delta k = k_{2\omega} - 2k_\omega = (2\omega/c)\Delta n$ is proportional to the index mismatch between the fundamental and harmonic frequencies. The absorption coefficient $\alpha_{2\omega}$ of the film at the harmonic frequency has been included in the analysis. Finally, $\chi_{\text{eff}}^{(2)}$ is the effective SHG susceptibility corresponding to the polarization configuration used in the experiment and it is expressed as³⁴

Configuration i [fundamental, X-polarized; second harmonic, Y-polarized]

$$\chi_{\text{eff}}^{(2)} = -\chi_{31}^{(2)} \sin \theta' = -\chi_{31}^{(2)} \frac{\sin \theta}{n_\omega} \quad (6a)$$

Configuration ii [fundamental, Y-polarized; second harmonic, Y-polarized]

$$\chi_{\text{eff}}^{(2)} = -[(2\chi_{15}^{(2)} + \chi_{31}^{(2)}) \cos^2 \theta' + \chi_{33}^{(2)} \sin^2 \theta'] \sin \theta' \quad (6b)$$

Configuration iii [fundamental, 45°-polarized; second harmonic, X-polarized]

$$\chi_{\text{eff}}^{(2)} = -\chi_{15}^{(2)} \sin \theta' = -\chi_{15}^{(2)} \frac{\sin \theta}{n_\omega} \quad (6c)$$

By fitting (5) and (6) to the experimental data, the values for the three nonzero components of the $\chi_{il}^{(2)}$ tensor have been independently determined. The susceptibilities measured for the three compounds after poling at 9 kV are listed in Table 1 together with the concentration in the films. Several conclusions can be immediately derived from the data:

(i) Susceptibility values for the three components are in the range 10^{-10} to 10^{-9} esu and so are quite significant. They are largest for compound **3** and smallest for compound **2** when normalized to equal concentration.

(ii) Slight departures from Kleinman symmetry are observed particularly for the phenyl- and trifluoromethylphenyl-substituted molecules (**2** and **3**). On the other hand, this symmetry rule is reasonably well-obeyed for the Cl-substituted compound **1**.

The ratio $r = \chi_{33}^{(2)}/\chi_{31}^{(2)}$ lies around 3 for the three compounds, i.e., is approximately in accordance with the behavior expected for low poling fields.

It is interesting to compare the above results for In-Pcs with those reported for some acceptor-substituted spin-coated films of subphthalocyanines^{28,29} (Figure 2), since both families of molecules are related to phthalocyanines and present similar pyramidal shapes. Reported values for the susceptibilities of those SubPc films are in the range from 4×10^{-10} to 8×10^{-10} esu for $\chi_{31}^{(2)}$, from -2×10^{-10} to -3×10^{-10} esu for $\chi_{15}^{(2)}$, and $\leq 1 \times 10^{-10}$ esu for $\chi_{33}^{(2)}$. From the comparison with the data for InPcs one first concludes that the off-axis components $\chi_{31}^{(2)}$ and $\chi_{15}^{(2)}$ reach similar values for the two families of compounds. However, a key difference between them is that, for SubPcs, $\chi_{33}^{(2)}$ is very small in relation to $\chi_{15}^{(2)}$ and $\chi_{31}^{(2)}$, which are of opposite sign. On the other hand, for InPcs, $\chi_{33}^{(2)}$ is around 3 times either $\chi_{31}^{(2)}$ or $\chi_{15}^{(2)}$. Although an explanation for these differences cannot be offered at this stage, we would like to point out the possible role of molecular symmetry (C_{3v} for SubPcs and C_{4v} for InPcs). For In-Pcs the planar Pc macrocycle has a C_{4v} point-group that is centrosymmetric, i.e., is not SHG active. Consequently, the SHG response of In-Pcs should originate from charge motion introduced by the perpendicular bond with the capping group. On the other hand, the C_{3v} plane in SubPcs already presents a nonzero nonlinear response that is purely octupolar. In this case an additional dipolar contribution could exclusively arise from the axial substituent. This may be the origin of the differences found between the two families of Pc-related compounds.

Finally, very large discrepancies from Kleinman symmetry were observed in subphthalocyanines. This should be very likely related to the strong resonant behavior at the second harmonic (532 nm) of SubPcs for fundamental light at $\lambda = 1064$ nm. That is not the case of In-Pcs where no appreciable absorption is observed at 532 nm (see Figure 4).

4. Summary and Conclusions

The quadratic hyperpolarizabilities of several axially substituted In–Pcs have been determined by EFISH at $\lambda = 1064$ nm. The electronic contribution to γ_{EFISH} has been evaluated through a two-level model (Q-band) and their contribution has been shown to be relevant. Obtained values are comparable to those measured for other peripherally substituted Pcs but smaller than those reported for the related family of pyramidal-shaped SubPcs. On the other hand, the three components $\chi_{15}^{(2)}$, $\chi_{31}^{(2)}$, and $\chi_{33}^{(2)}$ of the susceptibility tensor have been determined and reach significant values around 10^{-9} esu. At variance with SubPcs, where $\chi_{33}^{(2)} \approx 0$ ($\chi_{31}^{(2)}$ and $\chi_{15}^{(2)}$ present large values), for In–Pcs $\chi_{33}^{(2)}$ is the highest component and obeys $\chi_{33}^{(2)} \approx \chi_{31}^{(2)} \approx \chi_{15}^{(2)}$. The possible correlation of this fact with molecular symmetry has been pointed out.

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