# Third Harmonic Generation Spectroscopy of Boron Subphthalocyanine

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The dispersive behavior of the magnitude and phase of  $\chi^3(-3\omega:\omega,\omega,\omega)$  of sublimated boron subphthalocyanine (SubPc) thin films has been investigated via third harmonic generation (THG) spectroscopy in the range 950–2000 nm.  $\chi^3$  values, three times bigger than those obtained for phthalocyanines in the same frequency range, have been measured. A four-level model, including the ground state and three excited states associated to bands observed in the linear absorption spectrum, has been successfully used to explain the nonlinear behavior of these compounds.

### Introduction

Highly conjugated  $\pi$ -electron systems have been considered as the most suitable organic materials for third-order nonlinear optics.<sup>1</sup> Besides the conjugated polymers, metallorganic compounds are attracting growing interest due to their large thirdorder nonlinear optical responses.<sup>2</sup>

Metallophthalocyanines (MPcs),<sup>3</sup> two-dimensional 18  $\pi$ -electron conjugated macrocycles, have been intensively investigated for third-order nonlinear applications<sup>4-10</sup> due to their highly delocalized  $\pi$ -electron system. The chemical flexibility of phthalocyanines facilitates the tailoring of their electro-optical parameters in a very broad range. For this reason, modifications of Pcs are usually made by incorporating a wide variety of central metal ions, by peripheral substitution of the macrocycle,<sup>3</sup> or by preparation of analogues.<sup>3,11-13</sup>

Interesting examples of Pc-related compounds are the socalled subphthalocyanines (SubPcs, 1, Figure 1).<sup>14,15</sup> These macrocyclic complexes are composed of three isoindole units containing boron inside. They show a delocalized 14  $\pi$ -electron system similar to that present in Pcs.

Up to now the use of these compounds has been restricted to applications as intermediate materials for the synthesis of nonsymmetrical phthalocyanines.<sup>16–19</sup> Moreover, there are few reports published hitherto about the synthesis of SubPcs, probably due to their really difficult processes of purification.<sup>14–16,20</sup>

A previous X-ray crystallographic study<sup>15</sup> substantiated that SubPcs have a coned-shaped structure because of constraints arising from the coupling of the three isoindole units. However, spectral data reported by Kobayashi indicate that these molecules indeed have a strong aromaticity.<sup>20</sup> Other attractive characteristics of SubPcs, besides their large  $\pi$ -electron conjugation, are their chemical (they support inorganic acids) and thermal (they can be sublimated at 10<sup>-4</sup> mmHg at 350 °C) stability. These interesting features, as well as their singular geometry, prompted us to study their nonlinear optical properties in the context of our general project concerning the synthesis of Pcs and Pc analogues for nonlinear optical applications.<sup>21-23</sup>



Figure 1. Chemical structure of boron subphthalocyanine 1.

In this paper we report on the preparation and purification of large amounts of the previously described<sup>14</sup> SubPc 1 and on a detailed spectroscopic study of the magnitude and phase of the THG susceptibility  $\chi^3(-3\omega:\omega,\omega,\omega)$  of evaporated thin films of this compound. It should be noted that this susceptibility is purely electronic, being free from other contributions that affect the data obtained with alternative techniques such as degenerate four-wave mixing (DFWM)<sup>10</sup> or z-scan.<sup>5</sup>

### **Experimental Section**

Synthesis and Characterization. Compound 1 was characterized by elemental analysis, IR, and UV-visible spectroscopies, mass spectrometry and nuclear magnetic resonance spectroscopy. The UV-visible and infrared measurements were carried out on Perkin-Elmer model Lambda 6 and PU 9716 Philips spectrometers, respectively. The MS spectrum was determined on a MAT 900 (Finnigan MAT, GmbH, Bremen) instrument. The proton NMR spectrum was recorded with a Bruker WM-200-SY, 200 MHz spectrometer. The purity of the compound was determined on a Perkin Elmer Integral 4000 analytic high-performance liquid chromatographer Perkin Elmer Integral 4000 using toluene as mobile phase and a nucleosil 5-nitro column.

Synthesis of the Subphthalocyanine 1. A suspension of 12.8 g (0.1 mol) of dry phthalonitrile (recrystallized from methanol and dried in vacuum) in 12 mL of anhydrous 1-chloronaphthalene was magnetically stirred and cooled at -78 °C, in a 100 mL three-neck round-bottomed flask equipped with a thermo-

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meter, a reflux condenser, and a glass inlet tube for cannula introduction, under an argon atmosphere. Then, 4.3 mL (5.76 g, 50 mmol) of boron trichloride (previously condensed at -78°C) was added to the suspension by means of a cannula (with the help of a slightly positive argon pressure). The mixture was vigorously stirred at room temperature, and then an exothermic reaction took place with formation of a brown precipitate. The reaction mixture was heated at reflux temperature for 15 min. After being cooled, the mixture was diluted with methanol (50 mL) and the suspension filtered off by suction. Finally, the residue obtained was placed in the thimble of a soxhlet extractor and washed with methanol (250 mL) for 48 h. The residual bronze product was dissolved in sulfuric acid (100 mL) and reprecipitated with a mixture of ice-water. Yield: 4.33 g (30%). Mp > 300 °C. MS-EI (m/z): 430 (M<sup>+</sup>, 72), 395 (100), 265 (11), 215 (4), 197 (29), 139 (23), 128 (5). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 8.91, 7.96 (m, m, 6H, 6H,  $A_2B_2$  system). UV-visible  $\lambda_{max}/nm$  (log  $\epsilon$ , dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) (CHCl<sub>3</sub>) 565 (4.95), 524 (sh), 489 (sh), 305 (4.70).

SubPc thin films were prepared by vacuum sublimation over amorphous silica plates at 350 °C in a vacuum chamber at  $10^{-6}$ Torr. Their thicknesses (ranging between 300 and 400 nm) were measured on a profilometer (DEKTAK model 2).

Experimental THG Setup. The well-known Maker-fringe technique<sup>24</sup> was used to carry out tunable THG experiments in the 950-2000 nm spectral range.

The experimental setup used to access most of the wavelength ranges consisted of a frequency-doubled Q-switched Nd:YAG laser (10 Hz repetition rate) pumping a PDL-3 dye laser, which was then focused into an hydrogen Raman cell. Wavelengths from 1.264 to 1.414  $\mu$ m were obtained from the second Stokes shift of the Raman cell pumped with DCM dye, those in the 0.967–1.007 and 1.486–1.617  $\mu$ m regions from the first and second Stokes shifts, respectively, pumping with LDS 698, and finally, those in the 1.021–1.083 and 1.112–1.197  $\mu$ m regions, from the second Stokes shift, pumping respectively with Rhodamine 590 and Rhodamine 610. The range between 1.809 and 1.963  $\mu$ m was obtained by using a LiIO<sub>3</sub> INRAD downconverter, where the remaining 1.064  $\mu$ m was combined with the LDS 698 Dye laser beam. Additional wavelengths were obtained by pumping the Raman cell with the fundamental and second harmonic of the Nd:YAG laser.

The laser beam was focused onto the sample, which was placed into a 200 mTorr vacuum chamber, with the substrate always facing the photomultiplier.

The magnitude and phase of  $\chi^3$  were determined by fitting the data to the theoretical Maker-fringe expression.<sup>25</sup> Absorption at both the fundamental and the third harmonic was taken into account in the calculations.

Finally, the dispersive behavior of  $\chi^3$  was analyzed, by using expressions for  $\chi^3$  derived from perturbative methods by Orr and Ward.<sup>26,27</sup>

The measured macroscopic third-order susceptibility  $\chi^{3}_{zzzz}(-3\omega; \omega, \omega, \omega)$  for isotropic ensembles (assumed for our films), with z being the field polarization direction, is generally expressed<sup>6</sup> as

$$\chi^{3}_{zzzz}(-3\omega:\omega,\omega,\omega) = Nf\gamma_{g}(-3\omega:\omega,\omega,\omega)$$
(1)

where N is the molecular density, f is the Lorentz–Lorentz local field factor, and  $\gamma_g$  is the averaged molecular hyperpolarizability given by

$$\gamma_{g} = (1/5) \left[ \sum_{i} \gamma_{iiii} + (1/3) \sum_{i \neq j} (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}) \right]$$
(2)

where i and j are the molecular coordinates. For both linear



Figure 2. UV-visible spectrum of SubPc 1 in chloroform  $(1.2 \times 10^{-5} \text{ M})$ .

chains (with x along the molecular axis) and cyclic molecules such as phthalocyanines (with equivalent molecular x and y axes in the plane of the molecule), the dispersive behavior of  $\gamma_g$  is that of  $\gamma_{xxxx}$  with a factor of ( $^{1}/_{5}$ ) and ( $^{4}/_{5}$ ), respectively. The same applies to the SubPc, so in our analysis we assumed that the frequency dependence of the measured  $\chi^3$  is that of  $\gamma_{xxxx}$ 

### **Results and Discussion**

Although the synthesis of the SubPc was published by Meller and Ossko twenty years ago,<sup>14</sup> the purification process described therein was difficult to reproduce. In our hands the crude reaction mixture includes, besides side products from phthalonitrile degradation (easily removed by washing with methanol), compound 1 and also its mono- and dichloro derivatives (detected by HPLC and MS) as a consequence of aromatic chlorination by the action of boron trichloride. The three compounds sublimated together, but treatment with sulfuric acid and reprecipitation with water allowed us to obtain compound 1 in moderate yield although with 97% purity (tested by HPLC).

Compound 1 is soluble in chloroform and dichloromethane, but it is insoluble in other apolar organic solvents like hexane and in most of the polar ones, such as methanol. The solubility in chloroform allows us to analyze this compound by nuclear magnetic resonance showing a well defined  $A_2B_2$  system at 8.91 and 7.96 ppm.

The UV-visible spectrum of SubPc 1 in chloroform solution, similar to that of a metallophthalocyanine but shifted toward the blue, is dominated by two intense bands, one at 565 nm (Q band) and another one at 305 nm (Soret band) (Figure 2). A shoulder at around 520 nm is also observed, possibly associated with a vibronic transition. IR bands are in agreement with those described in the literature.<sup>14</sup> Similar UV-visible spectra, with some broadening, are observed in the thin films.

The experimental values for the magnitude and phase of the THG susceptibility  $\chi^3$  for SubPc 1 are respectively shown in Figure 3a and b. The dispersion curve for the magnitude of  $\chi^3$  ( $|\chi^3|$ ) presents two peaks centered at around 300 and 530 nm, in rough correlation with the linear absorption spectrum. This may suggest that only the electronic levels responsible for the linear bands play a significant role in the nonlinearity. It is important to note that experimental  $\chi^3$  values are three times higher than those obtained for phthalocyanines<sup>23</sup> in the same wavelength range, although the Q band for the SubPc has a higher transition energy and a lower extinction coefficient. This behavior should be related to the detailed electronic structure (not known at present) and will be next discussed in accordance with simple phenomenological three- and four-level models.

Firstly, we assumed a three-level model, including the ground state  $(|0\rangle)$  and two excited states  $(|1\rangle)$  and  $(|2\rangle)$  associated with

the two dominant bands of the linear spectrum (at 300 and 560 nm, respectively).

The expression for  $\chi^3$  (constants of eq 1 are omitted) for this three-level model would be

$$\chi^{3}(-3\omega;\omega,\omega,\omega) = -\mu_{01}^{4}D_{11} - \mu_{02}^{4}D_{22} - \mu_{01}^{2}\mu_{02}^{2}(D_{21}) + \mu_{12}^{2}(\mu_{01}^{2}D_{121} + \mu_{02}^{2}D_{212}) + \mu_{01}^{2}\Delta\mu_{01}^{2}D_{111} + \mu_{02}^{2}\Delta\mu_{02}^{2}D_{222} + \mu_{01}\Delta\mu_{01}\mu_{12}\mu_{20}D_{112} + \mu_{02}\mu_{21}\Delta\mu_{01}\mu_{10}D_{211} + \mu_{01}\mu_{12}\Delta\mu_{02}\mu_{20}D_{122} + \mu_{02}\Delta\mu_{02}\mu_{21}\mu_{10}D_{221}$$
(3)

where  $D_{ab}$  and  $D_{abc}$  are dispersive factors given by:

$$D_{ab} = (1/(\Omega_{a0} - 3\omega)(\Omega_{a0} - \omega)) + (1/(\Omega_{a0} - \omega)(\Omega_{b0}^{*} + \omega)(\Omega_{b0} - \omega)) + (1/(\Omega_{a0}^{*} + 3\omega)(\Omega_{b0}^{*} + \omega)) + (1/(\Omega_{a0}^{*} + \omega)(\Omega_{b0} - \omega)(\Omega_{b0}^{*} + \omega))$$
(4)

$$D_{abc} = (1/(\Omega_{a0} - 3\omega)(\Omega_{b0} - 2\omega)(\Omega_{c0} - \omega)) + (1/(\Omega_{a0}^* - \omega)(\Omega_{b0} + 2\omega)(\Omega_{c0} - \omega)) + (1/(\Omega_{a0}^* + 3\omega)(\Omega_{b0}^* + \omega)) + (1/(\Omega_{a0}^* + \omega)(\Omega_{b0}^* - 2\omega)(\Omega_{c0} - \omega)) + (1/(\Omega_{a0}^* + \omega)(\Omega_{b0}^* + 2\omega)(\Omega_{c0}^* + 3\omega))$$
(5)

Here  $\mu_{ab}$  is the dipolar moment for the  $|a\rangle \rightarrow |b\rangle$  transition and  $\Delta \mu_{0a}$  is the so-called mesomeric moment or difference between the ground and the excited state  $|a\rangle$  permanent dipole moments; that is,  $\Delta \mu_{0a} = \mu_{aa} - \mu_{00}$ ,  $\omega$  is the frequency of the applied optical field, and  $\Omega_{ab} = \omega_{ab} - i\Gamma_{ab}/2$ , where  $\omega_{ab}$  is the energy difference (in  $\hbar$  units) between states a and b ( $\omega_{ab} = 1/\lambda_{ab}^{max}$ ,  $\lambda_{ab}^{max}$  is the center of the absorption band associated with transition  $a \rightarrow b$ ) and  $\Gamma_{ab}$  is the fwhm.

It was experimentally determined (from capacitive and solvatochromic measurements) that no permanent dipole moments in both the ground and excited states are present, so in eq 3  $\Delta \mu_{0a} \approx 0$ , within the sensitivity of our setup (~0.5 D). This is reasonable in view of the strong aromaticity and that the molecular symmetry  $(C_{3\nu})$  may be considered close to  $D_3$ in relation to its electronic structure. A reasonable fit for the magnitude of  $\chi^3$  (Figure 3a) was then obtained when the only fitting parameter  $\mu_{12}$  (dipole moment between both excited states  $(|1\rangle)$  and  $(|2\rangle)$  was taken as 10 D. Nevertheless, the fit was very poor for the phase of  $\chi^3$  (Figure 3b). The only positive term in eq 3 is that proportional to  $\mu_{12}$ , which should dominate the nonlinearity if it is desirable to achieve a good fit for the phase of  $\chi^3$ . The influence of this term is introduced principally through the  $2\omega$  resonance with the band at 560 nm. The problem is that if this term is strong enough to fit the phase, then the fit for the magnitude becomes much worse (a peak at around 1200 nm, not found experimentally, dominates the nonlinearity). The importance of fitting both parameters, the magnitude and the phase, to test a given nonlinear model for the dispersive behavior of  $\chi^3$  has already been discussed in previous work with Pcs.23

Therefore, in order to improve the analysis, we considered the possibility of other electronic levels contributing to the nonlinearity. Two-photon states as those reported for phthalocyanines<sup>22,23</sup> cannot be invoked in this case, since no parityforbidden transitions exist, due to the non-centrosymmetry of the subphthalocyanine. Therefore, we took into account other possible allowed one-photon states, such as that associated with the shoulder observed in the linear absorption spectrum at around 520 nm.



**Figure 3.** (a, top) Relative (with respect to fused silica) magnitudes and (b, bottom) absolute phases (in deg) of  $\chi^3(3\omega)$  for sublimated subphthalocyanine 1 thin films. THG experimental results are represented by the open circles; the dashed line is the fit to a three-level model with  $\mu_{12} = 10$  D; the solid line is the best fit to a four-level model with  $\mu_{12} = 2$  D,  $\mu_{13} = 5$  D, and  $\mu_{23} = 10$  D.

A four-level model was then implemented including an additional state  $|3\rangle$  associated with the band at 520 nm. The expression for  $\chi^3$  in this case is

$$\chi^{3}(-3\omega;\omega,\omega,\omega) = -\mu_{01}^{4}D_{11} - \mu_{02}^{4}D_{22} - \mu_{03}^{4}D_{33} - \mu_{01}^{2}\mu_{02}^{2}(D_{12} + D_{21}) - \mu_{01}^{2}\mu_{03}^{2}(D_{13} + D_{31}) - \mu_{02}^{2}\mu_{03}^{2}(D_{23} + D_{32}) + \mu_{12}^{2}(\mu_{01}^{2}D_{121} + \mu_{02}^{2}D_{212}) + \mu_{13}^{2}(\mu_{01}^{2}D_{131} + \mu_{03}^{2}D_{313}) + \mu_{23}^{2}(\mu_{02}^{2}D_{232} + \mu_{03}^{2}D_{323}) + \mu_{01}\mu_{12}\mu_{23}\mu_{30}(D_{123} + D_{321}) + \mu_{01}\mu_{13}\mu_{32}\mu_{20}(D_{132} + D_{231}) + \mu_{02}\mu_{21}\mu_{13}\mu_{30}(D_{213} + D_{312})$$
(6)

 $\Delta \mu_{0a}$  values have already been omitted. Transition dipole moments  $\mu_{ab}$  have been considered to be real numbers, since the molecular Hamiltonian is invariant versus time inversion. Nevertheless, there is an uncertainity in the signs of the last three terms of eq 6.

Data were then fitted by using the three transition dipole moments  $\mu_{12}$ ,  $\mu_{13}$ , and  $\mu_{23}$  as fitting parameters. Figure 3 shows the best fit achieved with this four-level model with fitting parameters  $\mu_{12} = 2$  D,  $\mu_{13} = 5$  D, and  $\mu_{23} = 10$  D. All the other parameters used in the calculation were determined from

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the linear spectrum. Out of resonance the nonlinearity is dominated by the  $2\omega$  and  $3\omega$  resonances with the two levels at 520 and 560 nm, through the positive terms of eq 6. From the dipole transition moment values obtained from the fit, one sees that the state at 520 nm seems to play an important role in the nonlinearity. Nevertheless, it was checked that a simplified model with only this level or the two levels at 520 and 560 nm was not appropriate. Therefore, all three levels should be taken into account in order to properly fit experimental results.

An additional mechanism that may apply in our SubPc films is microscopic local field cascading. This idea is based on preliminary hyper-Rayleigh scattering (HLS) measurements on related SubPcs,<sup>28</sup> which have yielded high second-order hyperpolarizability  $\beta$  values due to their strong octupolar character, in addition to the high molecular density and the molecular asymmetry. Cascading was proposed by Meredith,<sup>29,30</sup> and it was successfully applied to account for the nonlinear optical properties of DANS ((dialkylamino)nitrostilbene) side chain polymers.<sup>31</sup> Unfortunately, in the models considered in this paper the dispersive behavior of the cascading term is essentially the same as those associated with the terms containing  $\mu_{12}, \mu_{13}$ , and  $\mu_{23}$ . Therefore, it has not been possible to confirm the operation of a cascading mechanism. A detailed study of  $\chi^3$  in films with a different concentration of subphthalocyanines (including data for solutions) as well as measurements of  $\beta$ , currently in progress, will help to identify the occurrence of a cascading contribution.

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