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# Subphthalocyanines: Novel Targets for Remarkable Second-Order Optical Nonlinearities

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**Figure 1.** Chemical structure of subphthalocyanines **1**−**3**.

The design and synthesis of new molecular and supramolecular systems for nonlinear optics (NLO) is currently of great scientific and technological interest.[1] Until now investigations on second-order nonlinear optical properties of organic molecules have concentrated mainly on one-dimensional dipolar systems. Recently, theoretical and experimental considerations have suggested the possibility of developing new synthetic approaches to molecules with nonlinearities of so-called "multipolar" origin.[2−5] In this communication we show that subphthalocyanines (SubPcs), $\pi$-conjugated phthalocyanine-related compounds, present very large second-order molecular polarizabilities ($\beta$) and emerge as novel targets for second-order nonlinear optical applications. Thus, for example the trinitro-SubPc **1**, described here for the first time, has shown experimental values of $\langle \beta^2 \rangle^{1/2}(2\omega) = 2000 \times 10^{-30}$ (static $\langle \beta^2(0) \rangle^{1/2} = 407 \times 10^{-30}$ esu) by hyper-Rayleigh scattering (HRS) experiments. These second-order polarizabilities are mostly associated with the octupolar contribution and are comparable to those found in the most efficient linear (or dipolar type) compounds, such as polyenes,[6] and to the best octupolar molecules described until now.

Phthalocyanines (Pcs) are two-dimensional macrocyclic 18-$\pi$-electron conjugated systems with a great variety of technological applications.[7] In the last years Pcs[8] and related analogues[9] have emerged also as a novel class of molecular materials for third-order NLO applications. SubPcs **1**−**3** (Figure 1) are Pc-related macrocyclic compounds formed by three coupled isoindole moieties having a delocalized 14-$\pi$-electron system.[10] Despite their cone-shaped structure,[11] these compounds have an aromatic nature.[12]

Few axially and peripherally substituted boron SubPcs[10,13−15] and dimers of SubPcs[12] have been described. Their NLO properties remain unexplored, except for a very recent study on the third-harmonic generation (THG) spectroscopy of an
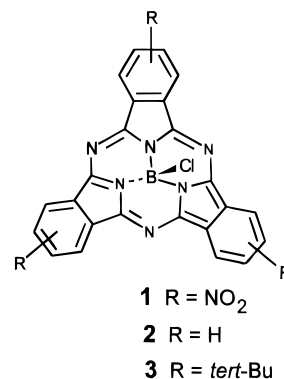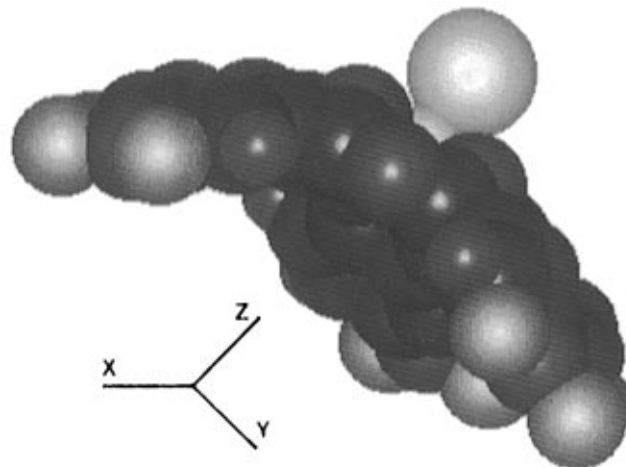


**Figure 2.** CPK model of compound **1** ($C_1$ symmetry isomer).

evaporated thin film of SubPc **2**,[16] where values of $\chi^{(3)}$, three times larger than those corresponding to Pcs in the same wavelength range, were measured. In that case, the possibility of "cascading mechanisms" related to important second-order NLO properties was suggested. Therefore, the main objective of this work has been to evaluate the potential of these new molecules for second-order NLO applications.

In this work we follow a 2D strategy for the design of SubPc-based NLO systems. Thus, besides the nonsubstituted SubPc **2**, we prepared SubPc **1**, with three surrounding strong acceptor substituents ($NO_2$) forming a trigonal arrangement (Figure 2), and SubPc **3**, having three peripheral donor groups (*tert*-Bu). Compounds **2**[10,16] and **3**[12] were prepared as previously described. Trinitro-SubPc **1** was synthesized for the first time in a similar way, by condensation of 4-nitro-1,2-dicyanobenzene in the pres-

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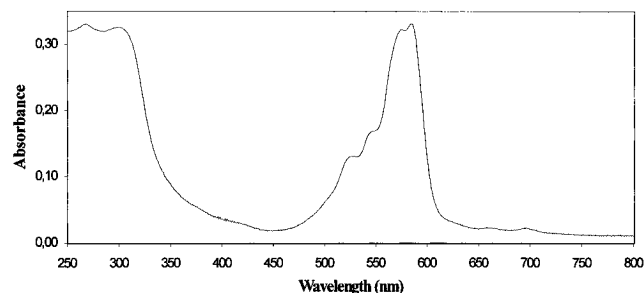
**Figure 3.** UV−visible spectrum of $(NO_2)_3SubPc$ **1**.

**Table 1.** Average Second- and Third-Order Polarizabilities $\langle\beta^2_{HRS}\rangle^{1/2}$ ($2\omega$) and $\langle\gamma_{EFISH}\rangle(2\omega)$, Determined Respectively from Hyper-Rayleigh Scattering (HRS) and Electric Field Induced Second Harmonic Generation (EFISH) Experiments for SubPcs **1−3**[a]

| compd | $\lambda_{max}$ (nm) | $\mu_0$ (D) | $\langle\gamma_{EFISH}\rangle(2\omega)$ ($\times 10^{-33}$ esu) | $\langle\beta^2_{HRS}\rangle^{1/2}$ ($2\omega$) ($\times 10^{-30}$ esu) | $\langle\beta^2_{HRS}(0)\rangle^{1/2}$ ($\times 10^{-30}$ esu) |
|---|---|---|---|---|---|
| **1** | 580 | 5.5 | −4 | 2000 | 407 |
| **2** | 565 | 0 | −6 | 296 | 71 |
| **3** | 570 | 1.3 | −3 | 380 | 86 |

[a] $\lambda_{max}$: Center of the principal linear absorption band. $\mu_0$: Ground state permanent dipole moment. $\langle\beta^2_{HRS}(0)\rangle^{1/2}$: Average static second-order polarizability, calculated from $\langle\beta^2_{HRS}\rangle^{1/2}$ ($2\omega$) by assuming a three-level model.

ence of boron trichloride using dry α-chloronaphthalene as solvent. The cyclotrimerization was carried out in this case at a remarkably low temperature (120 °C), thus producing **1** with high purity and good yield (80%).[17] The compound is soluble in moderate polar organic solvents like chloroform and in polar ones, such as methanol and acetone, giving an intense violet solution, but it is insoluble in hexane. By ^{1}H-NMR (500 MHz) and TOCSY bidimensional correlation experiments, SubPc **1** was shown to be a mixture of two structural isomers with $C_1$ (Figure 2) and $C_3$ symmetries in a 3:1 statistical distribution. The two isomers could not be separated by standard methods (HPLC, crystallization, etc.). The same 3:1 ratio of $C_1$ and $C_3$ isomers was found in compound **3** by ^{1}H-NMR and analytic HPLC.

The UV−visible spectra of SubPcs in chloroform are similar to those of Pcs, with two intense bands: one at around 580 nm (Q band), blue-shifted with respect to Pcs, and another one at around 305 nm (B band) (see Figure 3).[18]

The ground state dipole moments ($\mu_0$) were determined from capacitance measurements in toluene solutions by a classical method based on the Guggenheim theory.[19] The results (see Table 1) show the important difference between the nonsubstituted SubPc **2** ($\mu_0 = 0$) and the trinitro-substituted SubPc **1** ($\mu_0 = 5.3$ D). Then, measurements of the EFISH third-order polarizability $\gamma(-2\omega:\omega,\omega,0)$ were performed, using a standard setup.[20] The remarkable result was that $\gamma$ values (see Table 1) were essentially the same for all three SubPcs, in spite of the differences in $\mu_0$. This suggests that the vector part of the $\beta$ tensor is not important and should not yield any relevant harmonic intensity, the main contribution to the EFISH signal arising from the third-order $\gamma_e$ contribution. However, the

octupolar contribution still might be important and lead to large second-order NLO responses. Consequently, additional $\beta(-2\omega:\omega,\omega)$ measurements were performed in chloroform solution at 1.34 $\mu$m fundamental wavelength by the HRS technique,[21,22] giving the square root of the mean value of the $\beta$ tensor $\langle\beta^2\rangle^{1/2}$. Spectral analysis of the HRS signal around the harmonic wavelength ruled out the possibility of multipolar excited fluorescence. The experimental $\langle\beta^2\rangle^{1/2}(-2\omega)$ values for SubPcs **1−3** are reported in Table 1.

Firstly, one should note that even in the nonsubstituted SubPc **2**, with no dipolar contributions ($\mu_0 = 0$), $\beta$ is much higher than in traditional molecules such as *p*-nitroaniline.[1] The situation was similar for SubPc **3**, although in that case a small $\mu_0$ value was measured ($\mu_0 \approx 1.3$ D). On the other hand, for the trinitro-SubPc **1** $\beta$ is remarkably higher ($\beta = 2000 \times 10^{-30}$ esu). Since this larger value does not correlate with any similar enhancement in the EFISH results, one should conclude that it is associated with the octupolar (and not the dipolar) contribution. On the other hand, it is not clear whether octupolar $\beta$ values of $C_1$ and $C_3$ isomers are equal. Therefore, the reported values in Table 1 must be considered as "mean" values for the mixture of the two isomers.

Although the experiments were performed under nonabsorbing conditions (the harmonic frequency is far from the Q band), it is more relevant to report the static $\beta$ values (at zero frequency) for a correct assessment of our results. For such purpose, a quantum-mechanical microscopic model describing the dispersive behavior of $\beta$ needs to be implemented. A two-level model, often used for dipolar molecules, is not adequate for octupolar systems as it has already been discussed in previous works.[2,4] In the case of trigonal systems, like that of SubPcs, a three-level model has been proposed,[23] including the ground state $|0\rangle$ and a doubly degenerated excited state ($|1\rangle$ and $|2\rangle$). The dispersion of $\beta$ in such a model can be expressed as

$$\beta(\omega) = \frac{3|\mu_{01}|^2\mu_{12}}{\hbar^2\omega_{01}^2} \frac{\omega_{01}^2}{(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)} \quad (1)$$

where $\mu_{01}$ and $\omega_{01}$ are respectively the transition dipole moment and the frequency between the ground and excited states (associated with the Q band), $\omega$ is the frequency of the fundamental beam, and $\mu_{12}$ is the transition dipole moment connecting the two degenerate states.

Static $\beta(0)$ values calculated from eq 1 for SubPcs **1−3** are reported in Table 1. Although for SubPc **1** $\beta(0)$ becomes 1 order of magnitude lower than that experimentally obtained at 1.34 $\mu$m, it is still around 7 times larger than that corresponding to the nonsubstituted molecule (SubPc **2**).

The above $\beta$ values measured for the SubPcs are comparable to the most efficient second-order nonlinear compounds reported so far. The largest $\beta$ values of dipolar origin have been measured for highly conjugated linear molecules and polymers, such as polyenes, with static $\beta(0)$ as large as $911 \times 10^{-30}$ esu.[6] On the other hand, the most efficient octupolar molecule found in the literature is the $Ru^{II}$[tris(4,4′-*p*-dibutylaminostyryl-2,2′-bipyridine)], presenting a static $\langle\beta^2(0)\rangle^{1/2}$ value of $740 \times 10^{-30}$ esu.[5]

(17) SubPc **1**: deep blue powder, mp >300 °C (ethyl acetate−hexane). It was characterized by elemental analysis, IR and UV−visible spectroscopies, mass spectrometry [FAB-MS (*m/z* 566, M + H$^+$)], ^{1}H-NMR (500 MHz) and TOCSY bidimensional correlation experiments [three well-defined groups of signals (each 2 × d) appear centered at 9.78, 9.06, and 8.85 ppm (each 3H), respectively, corresponding to the three different kinds of highly deshielding aromatic protons of $C_1$ and $C_3$ isomers].

(18) In SubPc **1** the Q band (log $\epsilon$: 4.5) presents two peaks at 575 and 585 nm, which may be due to the presence of two isomers, and two shoulders at 528 and 547 nm. Two additional weak absorptions (log $\epsilon$: 3.4) appear at the low-energy side, at 659 and 696 nm.

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