

## ARTICLES

## Noncentrosymmetric Triazolephthalocyanines as Second-Order Nonlinear Optical Materials

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Three substituted triazolephthalocyanines, i.e., intrinsically noncentrosymmetric and planar phthalocyanine derivatives, have been synthesized and characterized. They present significant ( $\sim 10^{-28}$  esu) quadratic hyperpolarizabilities,  $\beta_{\text{HRS}}$  and  $\beta_{\text{EFISH}}$ , respectively measured at  $\lambda = 1.34 \mu\text{m}$  and  $\lambda = 1.907 \mu\text{m}$ . Moreover, the ratio  $\beta_{\text{EFISH}}^2(1.907 \mu\text{m})/(\beta_{\text{HRS}}^2(1.34 \mu\text{m}))$  markedly decreases when increasing the donor strength of the substituents at the isoindole rings (opposite to the triazole moiety). This has been attributed to the corresponding increase in the ratio  $\mu_{01}^x/\mu_{01}^z$  between the  $x$  (perpendicular to the molecular axis) and  $z$  (parallel to the molecular axis) in-plane components of the Q-band transition moment. This result suggests that the dipolar versus octupolar contribution to  $\beta$  could be varied and controlled by suitable selection of the donor/acceptor strength of the substituents.

## 1. Introduction

Second- and third-order nonlinear optical (NLO) materials are bound to play a key role in optoelectronics.<sup>1</sup> Existing technology mostly based on inorganic materials such as ferroelectric crystals (second order) and semiconductor materials and nanostructures (third-order) suffer from severe limitations, especially in terms of bandwidth, integrability and fabrication cost, and for this reason, during the last years, organic and polymer chemists have joined the quest for better electrooptic and nonlinear optical materials.<sup>2</sup> For third-order applications,<sup>3</sup> phthalocyanines<sup>4</sup> (Pcs) have emerged as very promising compounds due to their extended and highly polarizable two-dimensional  $\pi$ -electron system. Moreover, their electronic level structure is also favorable for optical limiting devices.<sup>3</sup> Unfortunately, most of the Pcs are centrosymmetric and therefore unsuitable for second-order NLO processes. However, the potential of Pc-related compounds for second-harmonic generation (SHG) has been recently pointed out<sup>5</sup> and some preliminary experiments have been performed.<sup>6–9</sup> One strategy for obtaining noncentrosymmetric systems involves the use of unsymmetrically substituted Pcs with suitable donor and acceptor groups. This approach has not been more extensively explored partly due to the difficulties in the preparation of these compounds.<sup>10</sup> Another possible route relies on the synthesis of intrinsically asymmetric Pc-related macrocycles. This is a novel strategy that has been followed in our present work, where the synthesis and

characterization of a series of substituted triazolephthalocyanines (Tpcs) is presented for the first time.

Tpcs<sup>11</sup> are core-modified phthalocyanines (Figure 1) in which one of the isoindole rings has been formally replaced by a 1,2,4-triazole moiety.<sup>11d</sup> Therefore, they are intrinsically unsymmetric 18  $\pi$ -electron fully conjugated metallomacrocycles with a potential for SHG. From a molecular design point of view, the acceptor character of the triazole subunit should lead to the polarization of the conjugated  $\pi$ -electron system, thus providing a strong dipolar moment to the molecule. To enhance this effect, donor groups have been added to the isoindole ring opposite to the triazole one. As an additional feature, these aromatic molecules are planar and provide an interesting example to discuss second-order NLO response in acentric conjugated two-dimensional systems, where not much information is available. For this case, off-diagonal components of the first-order hyperpolarizability tensor,  $\beta$ , should be very relevant and the balance between dipolar and octupolar contributions to the first-order hyperpolarizability should be markedly different from that found in linear one-dimensional systems.<sup>12</sup> For a meaningful description of the properties of these molecules, adequate, theoretical tools, which consider both diagonal and off-diagonal  $\beta$  components, are needed to analyze the data.<sup>13</sup> Finally, another positive feature is that Tpcs are also amphiphilic compounds particularly suitable for the preparation of in-plane oriented Langmuir–Blodgett films.<sup>14</sup>

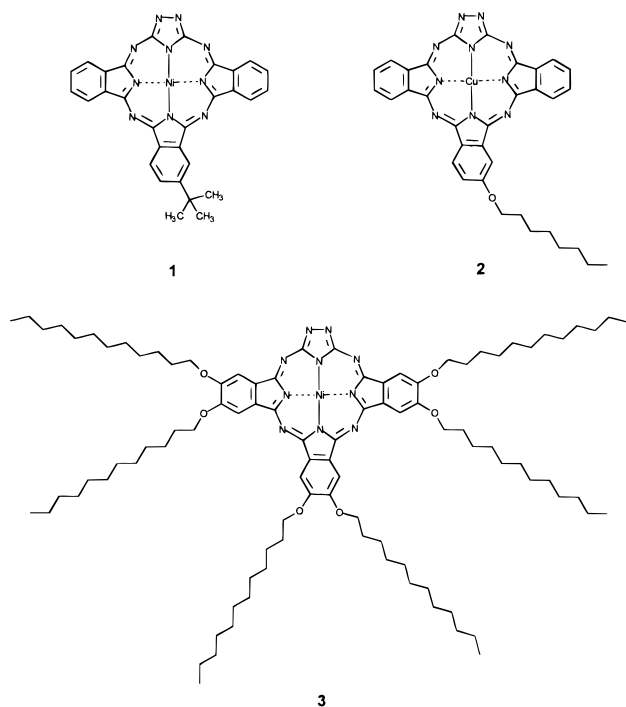
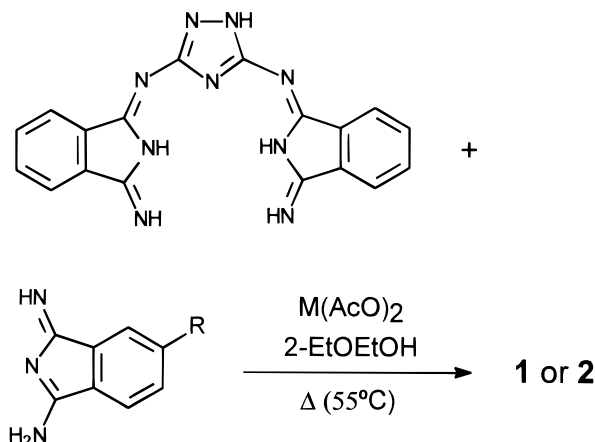


Figure 1. Chemical structure of triazolephthalocyanines 1–3.

#### SCHEME 1

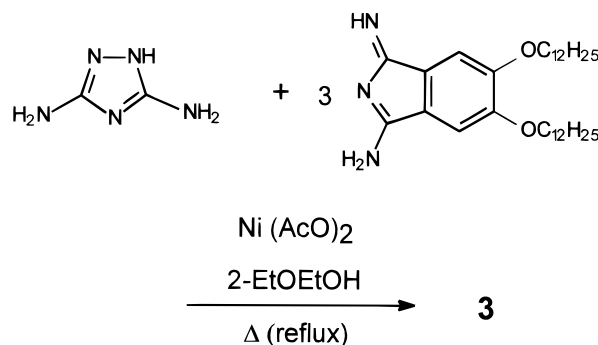


## 2. Experimental Section

**2.1. Synthesis.** Compounds **1**<sup>11b</sup> and **2** were synthesized by condensation reaction from 3,5-bis[(3-imino-1-isoindolinylidene)amino]-1,2,4-triazole,<sup>11d</sup> the appropriate 1,3-diiminoisoindoline, and the corresponding metal(II) acetate as template at 55 °C (Scheme 1). This one-pot method constitutes an improvement of the one previously described by us<sup>11b</sup> since in the present case the former preparation of the metal complex of 3,5-bis[(3-imino-1-isoindolinylidene)amino]-1,2,4-triazole<sup>11d</sup> is not required. This compound is most probably formed in situ by reaction of the 3,5-bis[(3-imino-1-isoindolinylidene)amino]-1,2,4-triazole<sup>11d</sup> with the metal salt and reacts in the same reaction conditions with the 1,3-diiminoisoindoline, affording **1** and **2** in higher yield (56%) than previously reported by us for **1** (46%). Both triazolephthalocyanines were purified by extraction in chloroform.

Compound **3** was prepared by following a statistical method, by reaction of 2,5-diamino-1,2,4-triazole (guanazole), 5,6-bis-(dodecyloxy)-1,3-diiminoisoindoline, and nickel(II) acetate in a 1:3:1 molar ratio at reflux of 2-ethoxyethanol (Scheme 2). Compound **3**, which is readily soluble in organic solvents due

#### SCHEME 2



to the presence of six aliphatic chains, was purified by column chromatography and fully characterized by elemental analysis and NMR, MALDI, IR, and UV–vis techniques.

**Synthesis of Compounds 1 and 2.** Compound **1** was prepared and purified in a similar way to compound **2**, with a 56% yield. It had been fully characterized previously.<sup>11b</sup>

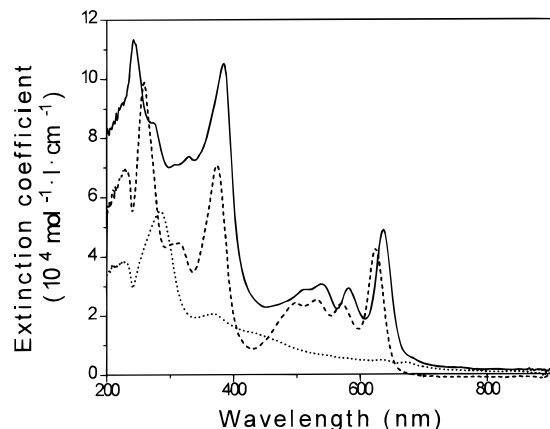
**9-(Octyloxy)-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo-[f,k,p][1,2,4,9,14,19]hexaazacycloeicosanate(2-)-N<sup>27</sup>,N<sup>28</sup>,N<sup>29</sup>,N<sup>30</sup> Copper(II) (2).** A mixture of 3,5-bis[(3-imino-1-isoindolinylidene)amino]-1,2,4-triazole<sup>11d</sup> (0.13 g, 0.37 mmol), Cu(AcO)<sub>2</sub> (0.074 g, 0.37 mmol), and 5-(octyloxy)-1,3-diiminoisoindoline (0.1 g, 0.37 mmol) in 2-ethoxyethanol (10 mL) was stirred at 55 °C for 6 days. After filtration, the raw material was triturated in methanol, and then the residue was repeatedly extracted with chloroform, to yield 0.15 g (62%) of **2**. Mp: >250 °C. MS-FAB (CH<sub>2</sub>Cl<sub>2</sub>), *m/z*: 656, 658 [(M + H)<sup>+</sup>, 100], 544, 546 [(M - C<sub>8</sub>H<sub>16</sub> + H)<sup>+</sup>, 50]. IR (KBr), *ν*: 3500–3200, 2924, 2855, 1588, 1496, 1473, 1420 (C≡N), 1366, 1328, 1290, 1237, 1115, 1099, 1076, 1008, 771, 763, 710 cm<sup>-1</sup> (C–H). UV–Vis, *λ* (log *ε*/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) (CHCl<sub>3</sub>): 242 (4.05), 269 (sh), 384 (4.02), 509 (sh), 541 (3.48), 582 (3.47), 637 nm (3.70). Anal. Calcd for C<sub>34</sub>H<sub>28</sub>N<sub>10</sub>OCu·2H<sub>2</sub>O: C, 58.99; H, 4.66; N, 20.23. Found: C, 58.56; H, 4.46; N, 20.53.

**2,3,9,10,16,17-Hexakis(dodecyloxy)-7,12:21,24-diimino-5,26:14,19-dinitrilotribenzo-[f,k,p][1,2,4,9,14,19]hexaazacycloeicosanate(2-)-N<sup>27</sup>,N<sup>28</sup>,N<sup>29</sup>,N<sup>30</sup> Nickel(II) (3).** A mixture of 5,6-bis(dodecyloxy)-1,3-diiminoisoindoline (0.83 g, 1.62 mmol), 3,5-diamino-1,2,4-triazole (0.053 g, 0.54 mmol), and Ni(AcO)<sub>2</sub>·4H<sub>2</sub>O (0.13 g, 0.54 mmol) was stirred in 2-ethoxyethanol (55 mL) at reflux for 24 h. After filtration, the raw material was triturated with methanol. Compound **3** was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>:MeOH, 20:1). Yield: 20%. Mp: >250 °C. <sup>1</sup>H NMR, *δ* (CDCl<sub>3</sub>): 7.6–6.5 (broad signal, 6H, H-arom), 4.1 (m, 12H, OCH<sub>2</sub>), 1.3 (broad signal, 126H, CH<sub>2</sub>), 0.9 ppm (m, 18H, CH<sub>3</sub>). <sup>13</sup>C RMN, *δ* (CDCl<sub>3</sub>): 32.0, 29.8, 26.3, 22.73 (CH<sub>2</sub>), 14.1 ppm (CH<sub>3</sub>). MS-MALDI (CHCl<sub>3</sub>), *m/z*: 1626 [(M+H)<sup>+</sup>]. IR (KBr), *ν*: 3600–3200, 2922, 2852, 1601, 1466 (C≡N), 1362, 1287, 1216, 1023, 861, 754 cm<sup>-1</sup> (C–H). UV–vis, *λ* (log *ε*/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) (CHCl<sub>3</sub>): 285 (4.75), 368 (4.32), 420 (sh), 632 (3.69), 673 nm (3.61). Anal. Calcd for C<sub>98</sub>H<sub>156</sub>N<sub>10</sub>O<sub>6</sub>Ni·2H<sub>2</sub>O: C, 70.69; H, 9.69; N, 8.41. Found: C, 70.01; H, 9.89; N, 8.95.

**2.2. Dipole Moments and Optical Properties: Experimental Details.** The permanent dipole moments in the ground state were experimentally obtained from capacitance measurements in chloroform solutions by a classical Guggenheim method.<sup>15</sup> Electric field induced second-harmonic (EFISH) experiments have been performed in chloroform solutions, as a function of the concentration at 1.907 μm fundamental wavelength. This wavelength is obtained by Raman shifting the 1.064 μm

**TABLE 1: Measured Cubic, Quadratic Hyperpolarizabilities and Permanent Ground-State Dipole Moment**

compd	$\mu^{(0)}$ (Debyes)	$\gamma_{\text{THG}}$ ( $10^{-33}$ esu) (1.34 $\mu\text{m}$ )	$\gamma_{\text{EFISH}}$ ( $10^{-33}$ esu) (1.907 $\mu\text{m}$ )	$\beta_{\text{EFISH}}$ ( $10^{-30}$ esu) (1.907 $\mu\text{m}$ )	$\sqrt{\langle\beta_{\text{HRS}}^2\rangle}$ ( $10^{-30}$ esu) (1.34 $\mu\text{m}$ )
<b>1ell</b>	6.4	−5.1	−3.2	−103	110
<b>2</b>	13.1	−7.6	−1.5	−24	80
<b>3</b>	14.1	−12.4	−0.5	−6.4	140

**Figure 2.** UV-vis spectra of compounds **1** ( $1.0 \times 10^{-5}$  M, dashed line), **2** ( $6.1 \times 10^{-6}$  M, solid line), and **3** ( $1.4 \times 10^{-5}$  M, dotted line) in chloroform solution.

emission of a nanosecond Q-switched Nd:YAG laser in a high-pressure hydrogen cell (60 bar). A liquid cell with thick windows in the wedge configuration<sup>16</sup> 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.

HRS experiments<sup>17</sup> were performed by measuring the intensity of the second-order scattered light on focusing an intense laser beam on the solution. The measurements were carried out at 1.34  $\mu\text{m}$ , which is directly emitted by another nanosecond Q-switched Nd: YAG laser.

The experimental setup for the third-harmonic generation (THG) experiment at 1.34  $\mu\text{m}$  is the same as the one used in EFISH experiments but in this case without an external electric field.

### 3. Results

**3.1. Dipole Moments.** The measured permanent ground-state dipole moments for the investigated Tpc molecules are given in Table 1. It is remarkable that they increase monotonically from compound **1** to **3** and reach high values for **2** and **3**, in correlation with the larger donor strength of the peripheral substituent groups.

**3.2. Linear Absorption Spectra.** Absorption spectra for compounds **1–3** in chloroform solution are displayed in Figure 2. Compounds **1** and **2** show characteristic bands at 630 and 370 nm, respectively, resembling the Q and B bands of Pcs<sup>4</sup> but shifted to shorter wavelengths. On the other hand, the absorption spectrum of compound **3** is markedly different. In particular, only a very small double band at 660–690 nm can be identified at the Q-band spectral region at a  $10^{-5}$  M concentration. At the B-band spectral region the absorption is also very low for this compound (particularly for the 380 nm component) in comparison with compounds **1** and **2** although it still remains quite significant. The peculiar optical behavior of compound **3** is related to the formation of molecular aggregates. Thus, the signals at 632 and 673 nm in the UV-visible spectrum of compound **3** show a slight red-shift and a

relative increase of intensity with regard to the other signals of the spectrum on going from  $10^{-5}$  to  $10^{-6}$  M concentrations of the sample in chloroform. This is consistent with a lower degree of aggregation upon dilution. However, at  $10^{-6}$  M concentration the quality of the spectrum is very poor and the still substantial difference with spectra of compounds **1** and **2** indicates that the aggregation remains even at this low concentration. Aggregation in phthalocyanines is a well-known phenomenon, which gives rise to broadening and blue shifting of the Q-band(s).<sup>4</sup> Therefore, the overall structure of the spectra can be more meaningfully discussed for compounds **1** and **2**. First, one notices that the extinction coefficients, particularly those referring to the Q-band, are lower for Tpcs than for Pcs. On the other hand, there is a clear red shift of the Q-band on moving from **1** to **2** (and possibly to **3**). Moreover, spectra for Tpcs present a rich structure between the B- and Q-bands with a number of new features whose origins are not clear. They probably arise from the splitting of the Q-band levels under the low-symmetry field generated by the molecular asymmetry. In fact, the new bands may account for the reduction in the area of the Q-band in comparison to Pcs. The additional structure is also apparent for compound **3**, although is not resolved. In view of the above data for the optical spectra, the discussion of the NLO results will be restricted to compounds **1** and **2**.

**3.3. NLO Responses.** The second-order NLO response has been determined through HyperRayleigh Light Scattering (HRS) and the measured  $\sqrt{\langle\beta_{\text{HRS}}^2\rangle}$  ( $=\beta_{\text{HRS}}$ ) values at  $\lambda = 1.34 \mu\text{m}$  are listed in Table 1. No multiphoton-induced luminescence has been detected at this wavelength. Reliable data could not be taken at 1.907  $\mu\text{m}$  (due to the low signal-to-noise ratio) where EFISH measurements were carried out (see below). The first-order hyperpolarizabilities are rather high and nearly resonant at  $2\omega$  with the Q-band. No significant differences in  $\beta_{\text{HRS}}$  are found between the three investigated compounds even though the overall absorption is strongly reduced for compound **3**. In fact, this compound shows the highest value for  $\beta_{\text{HRS}}$ . These values are only slightly lower than those reported for SubPcs, which are also intrinsically core-modified Pcs.<sup>9</sup> However, the  $\beta_{\text{HRS}}$  measured for Tpcs are higher than those reported for some noncentrosymmetric metalloporphyrins,<sup>18</sup> thus evidencing the stronger potential of this new synthetic route for NLO.

To provide additional information on the NLO response of Tpcs, third-harmonic generation and electric field induced second-harmonic experiments were performed. The values of the third-order molecular polarizability  $\gamma_{\text{THG}} = \gamma(3\omega; \omega, \omega, \omega)$  and  $\gamma_{\text{EFISH}} = \gamma(2\omega; 0, \omega, \omega)$  measured at  $\lambda = 1.34 \mu\text{m}$  and  $\lambda = 1.907 \mu\text{m}$ , respectively, are given in Table 1. The  $\gamma_{\text{THG}}$  values are negative and their absolute magnitudes are about 3 times lower than those for octasubstituted Pcs.<sup>19</sup> However, they are comparable or superior to those reported for unsymmetrically substituted Pcs<sup>7</sup> measured at the same wavelength. On the other hand,  $\gamma_{\text{EFISH}}$  show absolute values close to those of unsymmetrically substituted Pcs but with opposite, i.e., negative sign.<sup>7</sup> In a crude approximation one may neglect the electronic contribution to  $\gamma_{\text{EFISH}}$  and calculate the  $\beta_{\text{EFISH}}$  from the usual expression:  $\gamma_{\text{EFISH}} = \mu^{(0)}\beta_{\text{EFISH}}/5kT$ . This may be adequate since the fundamental and the second-harmonic wavelengths for the EFISH experiments ( $\lambda_{\omega} = 1.907 \mu\text{m}$  and  $\lambda_{2\omega} = 953.5 \text{ nm}$ ) are essentially off-resonant. The calculated values for  $\beta_{\text{EFISH}}$  are listed in Table 1 together with those measured by HRS ( $\beta_{\text{HRS}}$ ).

### 4. Discussion

As indicated at the end of section 3.2 the discussion of the NLO behavior will be restricted to compounds **1** and **2**, where



one is dealing with nonaggregated species. The focus will be on the different behavior inferred from HRS and EFISH data.

It is possible to qualitatively account for the discrepancy in  $\beta$  values from HRS and EFISH by recognizing the different tensorial contributions in both cases. Indeed, whereas  $\beta_{\text{EFISH}}$  is purely dipolar,  $\beta_{\text{HRS}}$  is made-up of both dipolar and octupolar contributions. The comparison between the EFISH and HRS values suggests that compound **1**, where  $\beta_{\text{EFISH}}^2/\langle\beta_{\text{HRS}}^2\rangle$  is larger, has a mostly dipolar component to  $\beta$  in correlation with the weak donor strength of the substituent group (opposite to the triazole moiety). On the other hand,  $\beta$  becomes multipolar, i.e., has an important octupolar component for compound **2**, where the substituent group shows a strong donor character. In fact, one should also mention that the ground-state dipole moment is much higher for compound **2** than for **1**.

For a quantitative comparison between the HRS and EFISH data one needs a specific model that takes into account the dispersive (wavelength dependent) behavior of the hyperpolarizabilities. To establish such a model is rather difficult due to the complexity of the absorption spectra of Tpcs. However, one may try a simplified energy-level scheme that helps to account for the experimental trends (not the absolute values) in the ratio  $\beta_{\text{EFISH}}^2/\langle\beta_{\text{HRS}}^2\rangle$ . First, it can be assumed that the B-band region (200–450 nm) does not make a substantial contribution to either the  $\beta_{\text{EFISH}}$  or  $\beta_{\text{HRS}}$  values. One can, therefore, use an effective two-level model associated with the Q-band (0, ground state and 1, excited state). Although the unsubstituted molecules display  $C_{2v}$  symmetry and so components of the transition moment  $\mu_{01}$  that are either parallel or perpendicular to the permanent dipole moment are exclusively allowed,<sup>12</sup> the substituents introduce some significant deviation from such strict symmetry group thus allowing both  $\mu_{01}^x$  and  $\mu_{01}^z$  components to be simultaneously nonzero. Then, the general expressions for  $\beta_{\text{EFISH}}$  and  $\langle\beta_{\text{HRS}}^2\rangle$ , for a planar molecular geometry, are given by

$$\beta_{\text{EFISH}} = \frac{\Delta m_{01}}{\hbar^2 \omega_{01}^2} \left[ (\mu_{01}^z)^2 + \frac{1}{3} (\mu_{01}^x)^2 \right] D_{\text{EFISH}} \quad (1)$$

where the  $z$  axis coincides with the direction of the mesomeric

$$\langle\beta_{\text{HRS}}^2\rangle = \left( \frac{\Delta m_{01}}{\hbar^2 \omega_{01}^2} \right)^2 [(\mu_{01}^z)^4 D_{\text{HRS},Z} + (\mu_{01}^x)^4 D_{\text{HRS},X} + (\mu_{01}^z)^2 (\mu_{01}^x)^2 D_{\text{HRS},ZX}] \quad (2)$$

$$\begin{cases} D_{\text{EFISH}} = {}^1\Omega + 2 \cdot {}^2\Omega \\ D_{\text{HRS},Z} = \frac{6}{35} ({}^1\Omega + 2 \cdot {}^2\Omega)^2 \\ D_{\text{HRS},X} = \frac{4}{35} ({}^1\Omega)^2 + \frac{2}{35} ({}^2\Omega \cdot {}^1\Omega) + \frac{20}{105} ({}^2\Omega)^2 \\ D_{\text{HRS},ZX} = \frac{2}{7} ({}^1\Omega)^2 + \frac{26}{35} ({}^2\Omega \cdot {}^1\Omega) + \frac{92}{105} ({}^2\Omega)^2 \end{cases} \quad (3)$$

$${}^1\Omega = \frac{\omega_{01}^2}{2(\omega_{01}^2 - \omega^2)} \quad {}^2\Omega = \frac{(\omega_{01}^2 + 2\omega^2)\omega_{01}^2}{2(\omega_{01}^2 - \omega^2)(\omega_{01}^2 - 4\omega^2)} \quad (4)$$

dipole moment  $\Delta m_{01}$  (difference between the permanent dipole moments of the ground and excited state) and  $x$  is the in-plane perpendicular component.

**TABLE 2: Ratio of Parallel and Perpendicular Components of the Transition Dipole Moments Inferred from the Ratio of the EFISH and HRS Quadratic Hyperpolarizabilities for Compounds 1 and 2**

compound	$\beta_{\text{EFISH}}^2(1.9 \mu\text{m})/\langle\beta_{\text{HRS}}^2(1.34 \mu\text{m})\rangle$	$\mu_{01}^x/\mu_{01}^z$
<b>1</b>	0.88	$\sim 0$
<b>2</b>	0.087	1.4

The ratio  $\mu_{01}^x/\mu_{01}^z$  can be calculated from the experimental value for the ratio  $\beta_{\text{EFISH}}^2/\langle\beta_{\text{HRS}}^2\rangle$ . The calculations have been carried out by exclusively considering the lowest energy component at the Q-band spectral region ( $\sim 630$  nm). The contribution of this component to both  $\beta_{\text{EFISH}}$  and  $\beta_{\text{HRS}}$  has been shown to be, indeed, dominant. More rigorous analysis should also take into account the other spectral components and a higher number of energy levels. In Table 2 we have listed the calculated values  $\mu_{01}^x/\mu_{01}^z$ , using the above-mentioned simplified model. The calculated values show a dominant perpendicular transition moment for compound **2** and a mostly parallel transition moment for compound **1** (for compound **3** the analysis cannot be reliably performed). This result gives support to the qualitative discussion advanced above and points out the role of the donor strength and geometrical arrangement of substituents on the NLO response. These effects are essentially two-dimensional and cannot be described within the usual one-dimensional framework. Polarized HRS measurements that would permit a more reliable assessment of  $||\beta_{J=3}||/||\beta_{J=1}||$  are being thus planned for future work.

## 5. Summary and Conclusions

In summary, intrinsically asymmetric Pc derivatives, Tpcs **1–3**, have been synthesized and characterized. They present significant SHG yields at the molecular level in relation to previous data on unsymmetrically substituted Pcs. An interesting additional feature of the results is that suitable peripheral substitution drastically alters the ratio between  $\beta_{\text{EFISH}}$  and  $\beta_{\text{HRS}}$ . The data have been analyzed using general two-dimensional expressions for  $\beta_{\text{HRS}}$  and  $\beta_{\text{EFISH}}$ . The increase in the ratio  $\beta_{\text{EFISH}}^2/\langle\beta_{\text{HRS}}^2\rangle$  upon moving from compound **2** to **1** is associated with the change in the transition dipole moment  $\mu_{01}$  from almost perpendicular to parallel to the molecular axis. Consequently, the relative importance of the dipolar and octupolar contributions can be controlled through chemical manipulation of the Pc macrocycle. To conclude, the above-mentioned properties, i.e., the significant SHG response, the tailoring of the multipolar character of the hyperpolarizability, the high dipolar moments, and the fact that triazolephthalocyanines can be organized in noncentrosymmetric condensed phases<sup>14</sup> and in discotic mesophases<sup>20</sup> make these Pc analogues attractive building blocks for the construction of molecular materials for nonlinear optics applications.

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