

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263576018>

# A critical evaluation of EFISH and THG non-linear optical responses of asymmetrically substituted meso-tetraphenyl porphyrins and their metal complexes

ARTICLE *in* INORGANICA CHIMICA ACTA · NOVEMBER 2002

Impact Factor: 2.05 · DOI: 10.1016/S0020-1693(02)01027-7

CITATIONS

20

READS

11

## 9 AUTHORS, INCLUDING:



**Maddalena Pizzotti**

University of Milan

92 PUBLICATIONS 1,546 CITATIONS

SEE PROFILE



**Silvio Quici**

Italian National Research Council

202 PUBLICATIONS 4,912 CITATIONS

SEE PROFILE



**Isabelle Ledoux-Rak**

Ecole normale supérieure de Cachan

84 PUBLICATIONS 938 CITATIONS

SEE PROFILE



**Giuseppe Zerbi**

Politecnico di Milano

492 PUBLICATIONS 10,788 CITATIONS

SEE PROFILE

# A critical evaluation of EFISH and THG non-linear optical responses of asymmetrically substituted *meso*-tetraphenyl porphyrins and their metal complexes

Maddalena Pizzotti<sup>a,\*</sup>, Renato Ugo<sup>a</sup>, Elisabetta Annoni<sup>a</sup>, Silvio Quici<sup>b</sup>,  
Isabelle Ledoux-Rak<sup>c</sup>, Giuseppe Zerbi<sup>d</sup>, Mirella Del Zoppo<sup>d</sup>, PierCarlo Fantucci<sup>e</sup>,  
Ivana Invernizzi<sup>e</sup>

<sup>a</sup> Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università e Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM),  
Università di Milano, Via G. Venezian 21, 20133 Milano, Italy

<sup>b</sup> Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM), Via Golgi 19, 20133 Milano, Italy

<sup>c</sup> Ecole Normale Supérieure de Cachan, 61 Avenue du Président Wilson, 94230 Cachan, France

<sup>d</sup> Dipartimento di Chimica Industriale, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

<sup>e</sup> Dipartimento di Biotecnologie e Bioscienze, Università di Milano Bicocca, Piazza della Scienza 2, 20126 Milano, Italy

Received 28 January 2002; accepted 15 April 2002

## Abstract

The experimental second and third order non-linear optical (NLO) responses  $\gamma_{\text{EFISH}}$  and  $\gamma_{\text{THG}}$ , measured working with a non-resonant incident wavelength of 1.907  $\mu\text{m}$ , of some push–pull *meso*-tetraphenyl porphyrins and their metal complexes, substituted in the *para* position of one phenyl ring with a nitro group and with hydrogen or methyl or methoxy groups in the *para* position of the other three phenyl rings, are critically discussed, also with the support of semiempirical MNDO–TDHF calculations. Care must be taken in evaluating the quadratic hyperpolarizabilities  $\beta_{\text{vec}}$  from  $\gamma_{\text{EFISH}}$  being the contribution of the cubic term  $\gamma_0(-2\omega; \omega, \omega, 0)$  to  $\gamma_{\text{EFISH}}$  not negligible at least when the second order NLO response is relatively low, as in porphyrins and their metal complexes investigated in this work. In addition experimental evidence has been produced that the value of  $\gamma_{\text{EFISH}}$  of the porphyrins and their metal complexes is increased by resonance enhancement when working with an incident wavelength of 1.34  $\mu\text{m}$ , due to the presence of very strong absorption bands in the region 0.400–0.650  $\mu\text{m}$  and that the  $\gamma_{\text{EFISH}}$  response is not significantly affected by  $3d^n$  ( $n = 7–10$ ) metal coordination. On the contrary  $\gamma_{\text{THG}}$  decreases by metal coordination due to the high resonance enhancement of  $\gamma_{\text{THG}}$  of free porphyrins. In fact the third harmonic  $3\omega$  (0.636  $\mu\text{m}$ ) in free porphyrins is quite close to some strong  $Q$  absorption bands above 0.615  $\mu\text{m}$ , which are lacking in the absorption spectra of their  $3d^n$  metal complexes. A vibrational method for the evaluation of the order of magnitude of the static cubic  $\gamma_0$  third order NLO response was successfully applied for the first time to a push–pull porphyrinic system.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Porphyrin complexes; Push–pull *meso*-tetraphenyl porphyrins; Non-linear optics

## 1. Introduction

Dipolar organic molecules with significant second order non-linear optical (NLO) properties have been extensively investigated in the last decades [1–3]. Only more recently symmetrical octupolar molecules have been studied with increasing interest [4], together with asymmetrical coordination and organometallic com-

pounds [5]. When compared to organic chromophores, coordination and organometallic chromophores offer additional electronic features which could act positively on the second order NLO response, such as strong charge transfer transitions (ligand to metal and vice-versa) at relatively low energy, which can be tuned by changing oxidation state, coordination sphere and stereochemistry thus producing additional flexibility to the design of a chromophore. In particular, cyclic ligands with a large  $\pi$  electronic system could potentially

\* Corresponding author. Fax: +39-02-583 554405

E-mail address: pizzotti@mailserver.unimi.it (M. Pizzotti).

act as a two dimensional highly polarizable electronic framework able to transmit charge transfer processes in push–pull systems. However, these large  $\pi$ -conjugated cyclic chromophores such as metallophthalocyanines [6] and metallotriazolohemiporphyrazines [7] show significant third order NLO responses, so their second order NLO responses, when low, cannot be correctly measured by the EFISH (Electric Field Induced Second Harmonic Generation) technique, due to a significant third order electronic contribution to the EFISH response [6,7].

Among these large  $\pi$ -delocalised chromophores, porphyrins and their metal complexes could offer some advantages for the synthesis of asymmetrical architectures [8]. As in phthalocyanines the high polarizability of the  $\pi$ -delocalised macrocycle of porphyrins is the origin of significant third order non-linearities, which have been extensively investigated [9]. Recent theoretical investigations have reached the conclusion that the correct substitution of the push–pull system in the porphyrin ring, characterised by strong intramolecular  $\pi$ – $\pi^*$  charge transfer transitions [10], and some specific electronic and structural properties of the push and pull groups could produce high second order responses [11], as it has been found experimentally by Therien and co-workers [12,13] and Ng and co-workers [14] who have investigated 5,15-diphenylporphyrins and their Zn(II), Cu(II) [12,13] or Ni(II) [14] complexes, carrying an electron releasing system ( $p$ -Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C≡C–) and a series of different electron withdrawing systems ( $p$ -NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C≡C– [12,13] or –CHO, –CH=C(CN)<sub>2</sub>, –CH=C(COOEt)<sub>2</sub>, *trans*-CH=CHCHO [14]) in the opposite 10, 20 meso positions. The quadratic hyperpolarizabilities  $\beta$  of these porphyrins and their metal complexes have been measured by Hyper-Rayleigh Scattering [12], Stark effect [13] and by EFISH [14]. Suslick et al. [15] have reported in a preliminary short communication, rather low second order NLO responses, measured by the EFISH technique, of push–pull *meso*-tetraphenyl porphyrins asymmetrically substituted in the *para* position of the phenyl rings with amino and nitro groups. However, nobody has pointed out clearly that due to the presence of strong absorption bands in the region 0.400–0.650  $\mu$ m [10] the quadratic hyperpolarizability  $\beta$  measured with any technique with an incident wavelength of 1.06 or 1.34  $\mu$ m could be affected by strong resonance enhancements, while in the EFISH measurements, even if carried out with a non-resonant incident wavelength of 1.907  $\mu$ m, the third order electronic contribution to  $\gamma_{\text{EFISH}}$  response could not, as in the case of phthalocyanines [6,7], neglected due to the already well-known large third order responses of porphyrins and their metal complexes [9]. Therefore, the experimental determination of the quadratic hyperpolarizability of porphyrins requires a more detailed and critical investigation. In order to give a

contribution to this particular point we investigated, due to their relatively easy synthesis, the experimental determination of second and third order NLO responses of a series of asymmetrical push–pull *meso*-tetraphenyl porphyrins (Fig. 1) with structural features similar to those of porphyrins studied by Suslick et al. [15] and of their metal complexes using the EFISH and THG (Third Harmonic Generation) techniques. In few cases we investigated also an easy and quick method for the determination of the order of magnitude of static second and third order NLO response, based on vibrational measurements, developed by some of us [16]. In parallel a theoretical investigation was carried out on the dipole moment values and at least on the order of magnitude of the EFISH and THG responses of these porphyrins and their Zn(II) complexes, based on the semiempirical MNDO (Modified Neglect of Diatomic Differential Overlap) method [17] coupled with the TDHF (Time Dependent Hartree-Fock) approach [18], as a tool to confirm the experimental trends and the presence of resonance enhancements in both EFISH and THG experimental measurements and how these responses can be affected by the presence of metal ions and their electronic structure.

The asymmetrically substituted push–pull *meso*-tetraphenyl porphyrins, investigated in this work, are reported in Fig. 1.

Only with the more asymmetrical porphyrin H<sub>2</sub>D the series of complexes with Co(II) (3d<sup>7</sup>), Ni(II) (3d<sup>8</sup>), Cu(II) (3d<sup>9</sup>), Zn(II) (3d<sup>10</sup>) ions and in parallel the series of complexes with Ni(II), Pd(II), Pt(II) (3d<sup>8</sup>, 4d<sup>8</sup>, 5d<sup>8</sup>) and Zn(II), Cd(II) (3d<sup>10</sup>, 4d<sup>10</sup>) ions were synthesized in order to investigate a possible effect due to the metal d electron configuration and to the energy of the  $nd^8$  ( $n = 3, 4, 5$ ) electron shell, respectively on the EFISH and THG responses.

## 2. Experimental

### 2.1. Spectroscopic determinations, dipole moments and NLO responses

<sup>1</sup>H NMR spectra were recorded on a Bruker AC-300 Spectrometer in CDCl<sub>3</sub> as solvent, UV–Vis spectra were

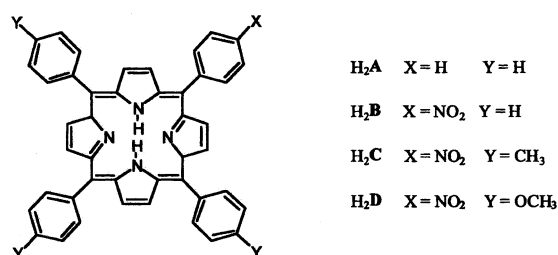


Fig. 1. Push–pull porphyrins studied in this work.

obtained in  $\text{CH}_2\text{Cl}_2$  with a Lambda 6 Perkin–Elmer Spectrometer.  $\text{FAB}^+$ -MS mass spectrometric measurements were performed with an analytical VG 7070 EQ instrument. THG and EFISH experiments have been performed in  $\text{CHCl}_3$  solutions, as a function of concentration ( $10^{-3}$ – $10^{-4}$  M), working at 1.34 and 1.907  $\mu\text{m}$  incident wavelengths, respectively, emitted by a Q-switched Nd:YAG laser with 60 and 20 ns pulse duration, respectively. The 1.907 fundamental wavelength was obtained by Raman shifting of the 1.064  $\mu\text{m}$  emission of the Q-switched Nd:YAG laser in a high pressure hydrogen cell (60 bar). A liquid cell with thick windows in the wedge configuration was used to obtain the Maker fringe pattern (harmonic intensity variation as a function of liquid cell translation) [19]. In the EFISH experiments the incident beam was synchronised with a DC field applied to the solution in order to break its centrosymmetry. From the concentration dependence of the harmonic signal with respect to that of the pure solvent, the NLO responses were determined (assumed to be real because the imaginary part was neglected). THG experiments provided the purely electronic cubic hyperpolarizability  $\gamma_{\text{THG}}(-3\omega; \omega, \omega, \omega)$  whereas EFISH experiments gave  $\gamma_{\text{EFISH}}$ , the sum of a cubic electronic contribution  $\gamma_0(-2\omega; \omega, \omega, 0)$  and of a quadratic orientational contribution  $\mu_0\beta_{\text{vec}}(-2\omega; \omega, \omega)/5$  kT, where  $\mu_0$  is the static dipole moment and  $\beta_{\text{vec}}$  the vectorial projection along the dipole moment direction of the tensorial quadratic hyperpolarizability (see later Eq. (3)) [20].

Experimental  $\gamma_{\text{THG}}$  were corrected from the absorption of  $3\omega$  by the  $Q$  absorptions bands [10], when these latter were close to  $3\omega$  (in particular in the case of free porphyrins). It follows that the absolute value of  $\gamma_{\text{THG}}$  may be affected by significant errors; therefore in the discussion we consider only the order of magnitude of  $\gamma_{\text{THG}}$ .

Experimental dipole moments determined in  $\text{CHCl}_3$  solutions following the Guggenheim method [21], were too low and not reproducible probably due to some aggregation of the dipolar disk-shaped porphyrin molecules at the concentrations required for capacitance and refractive index measurements.

## 2.2. Synthesis of asymmetrical porphyrins and their metal complexes

Porphyrins  $\text{H}_2\text{B}$ ,  $\text{H}_2\text{C}$  and  $\text{H}_2\text{D}$ , were prepared as reported below.  $\text{H}_2\text{A}$  was purchased from Aldrich Chemicals and used as received, elemental analyses were carried out in the Analytical Laboratories of Milan University.

### 2.2.1. 5-(4-Nitrophenyl)-10,15,20-tri-(4-methoxyphenyl)-porphyrin ( $\text{H}_2\text{D}$ )

A solution of 4-nitrobenzaldehyde (0.302 g, 2 mmol), 4-methoxybenzaldehyde (0.817 g, 6 mmol), pyrrole (0.536 g, 8 mmol) and trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ) (7.4 g, 65 mmol) in 800 ml of  $\text{CHCl}_3$  stabilised with 1% EtOH was stirred at room temperature (r.t.) for 20 h under nitrogen atmosphere and in the dark. After addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.82 g, 8 mmol) the reaction mixture was stirred for further 2 h, then  $\text{Et}_3\text{N}$  (7.26 g, 72 mmol) was added and the solvent evaporated. The residue was adsorbed on 50 g of Florisil and purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$  as eluant).

Porphyrin  $\text{H}_2\text{D}$  (320 mg, 21% yield) was separated as a purple powder, from *meso*-tetrakis-(4-methoxyphenyl)-porphyrin (21 mg) and *meso*-bis-(4-nitrophenyl)-bis-(4-methoxyphenyl)-porphyrin (130 mg) as a mixture of isomers.

### 2.2.2. 5-(4-Nitrophenyl)-10,15,20-tri-(4-methylphenyl)-porphyrin ( $\text{H}_2\text{C}$ )

Was prepared as  $\text{H}_2\text{D}$  from 4-nitrobenzaldehyde (0.302 g, 2 mmol), 4-methylbenzaldehyde (0.720 g, 6 mmol) and pyrrole (0.536 g, 8 mmol), yielding 370 mg of  $\text{H}_2\text{C}$  as a purple powder (26% yield), together with *meso*-tetrakis-(4-methylphenyl)-porphyrin (35 mg) and *meso*-bis-(4-nitrophenyl)-bis-(4-methylphenyl)-porphyrin (100 mg) as a mixture of isomers. It was crystallized from  $\text{CHCl}_3/\text{n-hexane}$ .

### 2.2.3. 5-(4-Nitrophenyl)-10,15,20-triphenylporphyrin ( $\text{H}_2\text{B}$ )

A solution of 4-nitrobenzaldehyde (0.302 g, 2 mmol), benzaldehyde (0.636 g, 6 mmol), pyrrole (0.536 g, 8 mmol) and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.84 g, 3 mmol) in 800 ml of  $\text{CH}_2\text{Cl}_2$  distilled over  $\text{K}_2\text{CO}_3$ , was stirred at r.t. for 20 h under nitrogen atmosphere and in the dark. After addition of DDQ (1.82 g, 8 mmol) the reaction mixture was stirred for further 2 h, then  $\text{Et}_3\text{N}$  (5 ml) was added and the solvent evaporated. The residue was adsorbed on 50 g of Florisil and purified by column chromatography (silica gel,  $\text{CHCl}_3$  as eluant). Porphyrin  $\text{H}_2\text{B}$  (300 mg, 25% yield) was separated as a purple powder, crystallized from  $\text{CHCl}_3/\text{n-hexane}$ , from *meso*-tetrakis-tetraphenylporphyrin ( $\text{H}_2\text{A}$ ) (112 mg) and *meso*-bis-(4-nitrophenyl)-bis-(phenyl)-porphyrin (130 mg) as a mixture of isomers.

Metal complexes of these porphyrins were obtained by their well established reactions with metal chlorides working in DMF as solvent [22].

In a typical preparation 100 mg of  $\text{H}_2\text{B}$  were dissolved in 20 ml of DMF, up to final dissolution. In a second time 53 mg of  $\text{PdCl}_2$  were added and dissolved by warming the mixture up to a solution which is kept under reflux for 3 h. The final reaction mixture was

diluted with 20 ml of cold water, the solid residue was filtered and washed with cold water. The solid was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$ , the suspension was filtered and the solvent evaporated under vacuum. The red residue was washed few times with *n*-pentane and then evaporated under vacuum, giving 106 mg (92% yield) of the palladium complex. While some complexes were isolated in enough pure form as red purple solids, other complexes (PdC, CoD, ZnD, CdD, PdD) were crystallized from  $\text{CH}_2\text{Cl}_2$ /*n*-hexane in order to obtain pure compounds. The platinum complex, which was obtained in relatively low yields starting from  $\text{PtCl}_2$ , was purified by column chromatography on  $\text{SiO}_2$  using  $\text{CH}_2\text{Cl}_2$  as eluant. The following yields (% in parenthesis) have been obtained: PdB (92), PdC (93), PdD (95), PtD (30), CoD (70), NiD (92), CuD (90), ZnD (90), CdD (60). In Table 1 are reported the analytical data and the relevant MS and  $^1\text{H}$  NMR data of both free porphyrins and the metal complexes synthesized.

### 2.3. Computational methods

The geometrical electronic structure of the porphyrinic macrocycles and their Zn complexes were investigated and dipole moments were calculated by the semiempirical MNDO method [17]. The NLO properties, both static and frequency dependent, were calculated by the direct time dependent HF approach (TDHF), as proposed by Sekino and Bartlett [18b,23] and by Karna and Dupuis [18a]. This approach does not require explicit calculations of excited states [24]. The MNDO calculations have been carried out using a standard version of MOPAC 6 program [25], to compute the best molecular geometry and wavefunction for the ground state, modified by us in order to include the coupled perturbed HF equations [26]. The modified NLO section of HONDO program [27], adapted by us to work with basic MNDO integrals, was used to calculate the NLO parameters.

Care must be taken when comparing calculated microscopic NLO response to those obtained experimentally by EFISH or THG techniques because the definition  $\gamma_{\text{EFISH}}$  and  $\gamma_{\text{THG}}$  is different if the Taylor series or the perturbation series convention are used [28]. In our theoretical approach use is made of Taylor expansion of both the energy and the induced dipole moments, in terms of the applied electric field. In addition the frequency dependent operators are all treated in an exponential form, instead of a cosine expansion. Both aspects require specific numerical corrections (0.5 for  $\beta_{\text{vec}}$  and 0.133 for  $\gamma_{\text{EFISH}}$ ,  $\gamma_{\text{THG}}$  and  $\gamma_0$ ) in order to compare the computed values with the experimental EFISH or THG measurements, defined according to so called ‘phenomenological’ convention [28].

### 2.4. Vibrational method for evaluation of NLO properties

NLO properties of polyconjugated  $\pi$ -delocalised structures may be evaluated by means of vibrational observables due to the very large electron–photon coupling which characterizes these peculiar highly  $\pi$ -conjugated molecules. Under this condition a reliable estimate of both second and third order NLO responses is given just by the contribution of nuclear relaxations, according to the Eqs. (1) and (2), derived under the hypothesis of both mechanical and electrical harmonicity [16]:

$$\beta_{nmp}^{\Gamma} = \frac{1}{4\pi^2 c^2} \sum_k \left( \frac{1}{v_k^2} \right) \left[ \left( \frac{\delta\mu_n}{\delta Q_k} \right) \left( \frac{\delta\alpha_{mp}}{\delta Q_k} \right) + \left( \frac{\delta\mu_m}{\delta Q_k} \right) \left( \frac{\delta\alpha_{np}}{\delta Q_k} \right) + \left( \frac{\delta\mu_p}{\delta Q_k} \right) \left( \frac{\delta\alpha_{nm}}{\delta Q_k} \right) \right] \quad (1)$$

$$\gamma_{nmps}^{\Gamma} = \frac{1}{4\pi^2 c^2} \sum_k \left( \frac{1}{v_k^2} \right) \left( \frac{\delta\mu_n}{\delta Q_k} \right) \left( \frac{\delta\beta_{mps}}{\delta Q_k} \right) + \left( \frac{\delta\mu_m}{\delta Q_k} \right) \times \left( \frac{\delta\beta_{nps}}{\delta Q_k} \right) + \left( \frac{\delta\mu_p}{\delta Q_k} \right) \left( \frac{\delta\beta_{nms}}{\delta Q_k} \right) + \left( \frac{\delta\mu_s}{\delta Q_k} \right) \left( \frac{\delta\beta_{nmp}}{\delta Q_k} \right) + \left( \frac{\delta\alpha_{nm}}{\delta Q_k} \right) \left( \frac{\delta\alpha_{ps}}{\delta Q_k} \right) + \left( \frac{\delta\alpha_{np}}{\delta Q_k} \right) \left( \frac{\delta\alpha_{ms}}{\delta Q_k} \right) + \left( \frac{\delta\alpha_{ns}}{\delta Q_k} \right) \left( \frac{\delta\alpha_{mp}}{\delta Q_k} \right) \quad (2)$$

The quantities such as  $\delta\mu_n/\delta Q_k$ ,  $\delta\alpha_{nm}/\delta Q_k$ ,  $\delta\beta_{nms}/\delta Q_k$  (where *n*, *m*, *s* and *p* indicate the Cartesian components), were obtained from infrared intensities and Raman or Hyper Raman cross sections, respectively (where  $v_k$  is the vibrational frequency of the *k*th normal mode  $Q_k$ ) giving purely *static* molecular NLO properties.

Raman data have been obtained with a Nicolet Raman 910 with exciting line at 1.064  $\mu\text{m}$  (resolution 4  $\text{cm}^{-1}$ ). Infrared spectra were recorded on a Nicolet FTIR Spectrometer System 800 (resolution 1  $\text{cm}^{-1}$ ).

## 3. Results and discussion

### 3.1. Synthesis of porphyrins and their metal complexes

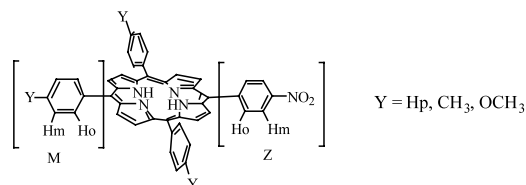
The synthesis of the asymmetrically substituted porphyrins  $\text{H}_2\text{B}$ ,  $\text{H}_2\text{C}$ ,  $\text{H}_2\text{D}$  was achieved by performing the general synthetic procedure described by Lindsey and co-workers [29a] (see Section 2). The distribution of the reaction products occurs in a statistical way, as recently described by other authors [29b], giving place to a mixture of porphyrins (Fig. 2) which can be easily separated by chromatography. The metal complexes were synthesized in DMF by reaction of the porphyrin with the metal salt, following the reported general synthetic procedure [22]. All attempts to isolate the complex of  $\text{H}_2\text{D}$  with the  $\text{Hg(II)}$  ion failed starting either

Table 1  
Analytical data (elemental analyses, mass spectra and  $^1\text{H}$  NMR spectra) of porphyrins  $\text{H}_2\text{B}$ ,  $\text{H}_2\text{C}$ ,  $\text{H}_2\text{D}$  and their metal complexes

Compound	Elemental analysis <sup>a</sup>			MS-FAB(+) ( <i>m/z</i> )	$^1\text{H}$ NMR ( $\text{CDCl}_3$ ) <sup>b,c</sup> $\delta$ (ppm)
	C(%)	H(%)	N(%)		
$\text{H}_2\text{B}$	79.51 (80.08)	3.98 (4.44)	10.45 (10.62)	659	–2.8 (s, 2H, NH); 7.70–7.82 [m, 9H, $\text{H}_\text{o}$ , $\text{H}_\text{p}$ (M)]; 8.21 [dd, 6H, $\text{H}_\text{m}$ (M)]; 8.39 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.63 [d, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.6$ Hz]; 8.73 [d, 2H, $\text{H}_\text{p}$ (Z)]; 8.86 [s, 4H, $\text{H}_\text{p}$ (M)]; 8.89 [d, 2H, $\text{H}_\text{p}$ (Z)]; $J_{\text{H}_\text{p},\text{H}_\text{o}} = 4.8$ Hz]
$\text{PdB}$	69.42 (69.13)	3.06 (3.57)	8.67(9.23)	763	7.70–7.82 [m, 9H, $\text{H}_\text{o}$ , $\text{H}_\text{p}$ (M)]; 8.16 [d, 6H, $\text{H}_\text{m}$ (M)]; 8.33 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.59 [d, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.3$ Hz]; 8.68 [d, 2H, $\text{H}_\text{p}$ (Z)]; 8.82 [s, 4H, $\text{H}_\text{p}$ (M)]; 8.85 [d, 2H, $\text{H}_\text{p}$ (Z)]; $J_{\text{H}_\text{p},\text{H}_\text{o}} = 5.0$ Hz]
$\text{H}_2\text{C}$	80.20 (80.41)	4.59 (5.04)	10.10 (9.99)	701	–2.75 (s, 2H, NH); 2.70 (s, 9H, $\text{CH}_3$ ); 7.56 [d, 6H, $\text{H}_\text{o}$ (M)]; 8.09 [d, 6H, $\text{H}_\text{m}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 7.7$ Hz]; 8.38 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.62 [d, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.6$ Hz]; 8.71 [d, 2H, $\text{H}_\text{p}$ (Z)]; 8.87 [s, 4H, $\text{H}_\text{p}$ (M)]; 8.91 [d, 2H, $\text{H}_\text{p}$ (Z)]; $J_{\text{H}_\text{p},\text{H}_\text{o}} = 4.8$ Hz]
$\text{PdC}$	69.72 (69.99)	3.92 (4.14)	8.72 (8.69)	806	2.70 (s, 9H, $\text{CH}_3$ ); 7.54 [d, 6H, $\text{H}_\text{o}$ (M)]; 8.03 [d, 2H, $\text{H}_\text{m}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 7.8$ Hz]; 8.34 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.60 [d, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.6$ Hz]; 8.66 [d, 2H, $\text{H}_\text{p}$ (Z)]; 8.83 [s, 4H, $\text{H}_\text{p}$ (M)]; 8.87 [d, 2H, $\text{H}_\text{p}$ (Z)]; $J_{\text{H}_\text{p},\text{H}_\text{o}} = 5.0$ Hz]
$\text{H}_2\text{D}$	74.83 (75.27)	4.40 (4.71)	9.40 (9.34)	750	–2.75 (s, 2H, NH); 4.10 (s, 9H, $\text{OCH}_3$ ); 7.29 [d, 6H, $\text{H}_\text{o}$ (M)]; 8.11 (d, 6H, $\text{H}_\text{m}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.6$ Hz]; 8.39 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.63 [dd, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.5$ ; $J_{\text{H}_\text{o},\text{H}_\text{p}} = 4.0$ Hz]; 8.70–9.00 (m, 8H, $\text{H}_\text{p}$ ).
$\text{CoD}$	69.80 (69.94)	4.34 (4.13)	8.75 (8.71)	807	Paramagnetic
$\text{CuD}$	69.08 (69.57)	3.71 (4.11)	8.72 (8.63)	811	Paramagnetic
$\text{ZnD}$	70.11 (69.39)	3.99 (4.10)	8.86 (8.64)	813	4.10 (s, 9H, $\text{OCH}_3$ ); 7.28 [d, 6H, $\text{H}_\text{o}$ (M)]; 8.11 [(d, 6H, $\text{H}_\text{m}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 7.9$ Hz]; 8.39 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.63 [dd, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.4$ ; $J_{\text{H}_\text{o},\text{H}_\text{p}} = 3.4$ Hz]; 8.80–9.08 (m, 8H, $\text{H}_\text{p}$ )
$\text{CdD}$	65.55 (65.62)	4.09 (3.87)	8.57 (8.14)	860	4.10 (s, 9H, $\text{OCH}_3$ ); 7.25–7.30 [m, 6H, $\text{H}_\text{o}$ (M)]; 7.85–7.95 [m, 6H, $\text{H}_\text{m}$ (M)]; 8.12–8.20 [m, 2H, $\text{H}_\text{m}$ (Z)]; 8.35–8.45 [m, 2H, $\text{H}_\text{o}$ (Z)]; 8.48–8.62 (m, 8H, $\text{H}_\text{p}$ )
$\text{NiD}$	69.57 (69.96)	4.24 (4.13)	8.45 (8.71)	805	4.05 (s, 9H, $\text{OCH}_3$ ); 7.20 [d, 6H, $\text{H}_\text{o}$ (M)]; 7.90 [d, 6H, $\text{H}_\text{m}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.0$ Hz]; 8.17 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.54 [dd, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.3$ ; $J_{\text{H}_\text{o},\text{H}_\text{p}} = 3.5$ Hz]; 8.56–8.85 (m, 8H, $\text{H}_\text{p}$ )
$\text{PdD}$	65.94 (66.02)	3.78 (3.90)	8.25 (8.20)	854	4.05 (s, 9H, $\text{OCH}_3$ ); 7.27 [d, 6H, $\text{H}_\text{o}$ (M)]; 8.06 (d, 6H, $\text{H}_\text{m}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.1$ Hz]; 8.34 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.62 [dd, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.2$ ; $J_{\text{H}_\text{o},\text{H}_\text{p}} = 3.4$ Hz]; 8.65–8.92 (m, 8H, $\text{H}_\text{p}$ )
$\text{PtD}$	59.78 (59.81)	3.04 (3.53)	7.39 (7.47)	942	4.10 (s, 9H, $\text{OCH}_3$ ); 7.25 [dd, 6H, $\text{H}_\text{o}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{p}} = 3.0$ Hz]; 8.04 (d, 6H, $\text{H}_\text{m}$ (M)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.3$ Hz]; 8.32 [d, 2H, $\text{H}_\text{m}$ (Z)]; 8.58 [dd, 2H, $\text{H}_\text{o}$ (Z)]; $J_{\text{H}_\text{o},\text{H}_\text{m}} = 8.5$ ; $J_{\text{H}_\text{o},\text{H}_\text{p}} = 3.6$ Hz]; 8.65–8.90 (m, 8H, $\text{H}_\text{p}$ )

<sup>a</sup> Theoretical values in parenthesis.

<sup>b</sup>



<sup>c</sup>  $\text{H}_\text{p}$  are the pyrrolic protons in the  $\beta$  position.



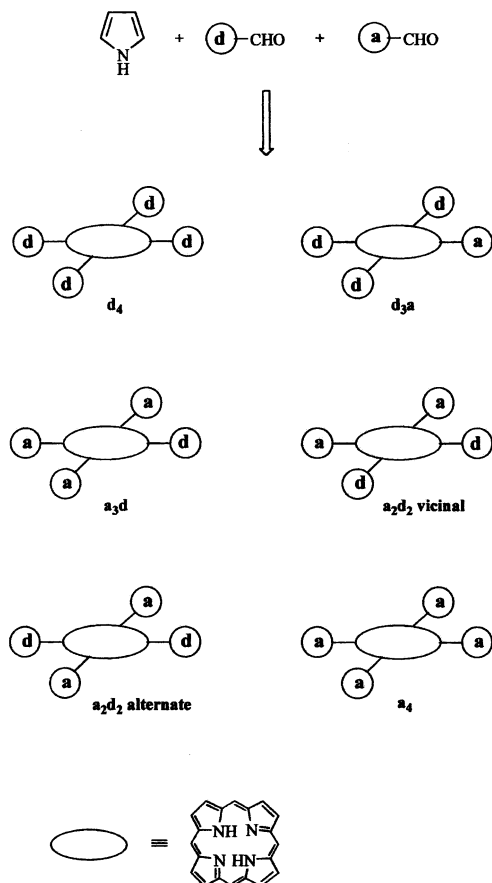


Fig. 2. Distribution of products of a mixed condensation of two aldehydes with pyrrole (d, donor group; a, acceptor group).

from HgO, Hg(CH<sub>3</sub>COO)<sub>2</sub> or other Hg(II) compounds, while the complex of the same porphyrin with the Cd(II) ion was obtained only in low yield, although it was reported that both complexes should be prepared easily following this general synthetic procedure [22]. Also the synthesis of the Pt(II) complex of H<sub>2</sub>D was not straightforward. For instance it cannot be obtained in acceptable yields starting from Na<sub>2</sub>[PtCl<sub>4</sub>]. Even using as a starting material PtCl<sub>2</sub> yields are rather low and chromatographic purification is required (see Section 2).

### 3.2. Electronic spectra and dipole moments

The electronic absorptions spectra of free porphyrins H<sub>2</sub>A, H<sub>2</sub>B, H<sub>2</sub>C and H<sub>2</sub>D and their metal complexes, characterized as expected [10] by a very strong Soret absorption band ( $\epsilon$  about  $10^5$  M<sup>-1</sup> cm<sup>-1</sup>) at about 400 nm and by some other weaker, although still strong, Q bands ( $\epsilon$  about  $10^4$  M<sup>-1</sup> cm<sup>-1</sup>) in the region 500–650 nm are not too influenced by the different molecular asymmetry of our push–pull systems (see Table 2). The introduction of a metal produces, as reported [10], a lower number of Q absorption bands together with the complete disappearance of those above 615 nm (Table 2).

Table 2  
Absorption electronic spectra in CH<sub>2</sub>Cl<sub>2</sub>

Compound	$\lambda_{\max}$ nm (log $\epsilon$ M <sup>-1</sup> cm <sup>-1</sup> ) B bands	$\lambda_{\max}$ nm (log $\epsilon$ M <sup>-1</sup> cm <sup>-1</sup> ) Q bands
H <sub>2</sub> A	411(5.11)	483sh (3.53), 514 (4.24), 549 (3.86), 588 (3.64), 646 (3.59)
H <sub>2</sub> B	412(5.34)	515 (4.32), 550 (3.99), 590 (3.81), 647 (3.66)
PdB	416(5.47)	485 (3.52), 524 (4.48), 555 (3.52)
H <sub>2</sub> C	416(5.23)	517 (4.20), 553 (3.95), 591 (3.67), 647 (3.61)
PdC	415(5.29)	524 (4.34), 555 (3.48)
ZnC	421(5.25)	551 (4.29), 560 (3.89)
H <sub>2</sub> D	419(5.17)	520 (4.04), 556 (3.87), 594 (3.54), 650 (3.56)
CoD	414(5.26)	531 (4.13)
CuD	417(5.26)	504 (3.48), 542 (4.24), 580(3.49)
ZnD	423(5.39)	515 (3.56), 552 (4.23), 593 (3.79)
CdD	436(5.44)	530 (3.64), 570 (4.23), 614 (4.16)
NiD	419(5.29)	531 (4.26), 615 (2.91)
PdD	418(5.30)	488 (3.53), 526 (4.42), 560 (3.55)
PtD	406(5.35)	512 (4.39), 540 (3.67)

Evidence of a fluorescent behaviour [10] can be reached even visually: the CdD complex is red–violet in the solid state, whilst in chloroform solution it appears to be violet but with a strong dominating green fluorescent emission.

Ground state dipole moments, which could not be safely measured in CHCl<sub>3</sub> solution by the standard Guggenheim method [21] (see Section 2) were calculated by using the MNDO semiempirical method [17]. Calculated dipole moments are quite similar (around 6D) and they do not change when free and complexed porphyrins are compared (Table 3). However, when the donor group is NH<sub>2</sub> the calculated dipole moment increases up to 9 D (Table 3), a value higher than the experimental value of  $5 \pm 1$  D reported by Suslick et al. [15]. This latter experimental data however could be low due to some aggregation of the porphyrin in CHCl<sub>3</sub> solution (see Section 2). Even if our calculated dipole moments are probably overestimated, they seem to be quite low, differently from the dipole moments of some asymmetrical phthalocyanines with peripheral substitution of the macrocycle with donor and acceptor groups [30]. For instance they are not much higher than just the vectorial sum of the dipole moments of nitrobenzene and of benzene substituted with the various donor groups (NH<sub>2</sub>, CH<sub>3</sub>O, CH<sub>3</sub>) (Table 3) [31]. Therefore, calculated dipole moments of these push–pull architectures confirm a lack of significant electronic exchange between the substituents on the phenyl rings via the porphyrin macrocycle [15], in agreement with the observation that in H<sub>2</sub>B, H<sub>2</sub>C, H<sub>2</sub>D, ZnB, ZnC, ZnD, the calculated negative charge located on the NO<sub>2</sub> group (−0.18) remains quite independent upon the nature of

Table 3  
Calculated dipole moments

Compound	$\mu_{\text{calc}}(\text{D})^{\text{a,d}}$	Sum of $\mu(\text{C}_6\text{H}_5\text{NO}_2) + \mu(\text{C}_6\text{H}_5\text{X}) (\text{D})^{\text{b,c}}$
H <sub>2</sub> B	6.7	4.03 (X = H)
ZnB	6.2	
H <sub>2</sub> C	6.7	4.58 (X = CH <sub>3</sub> )
ZnC	6.1	
H <sub>2</sub> D	6.3	5.28 (X = OCH <sub>3</sub> )
ZnD	6.4	

<sup>a</sup> Calculated by using the MNDO semiempirical method (see Section 2.3).

<sup>b</sup> Obtained from Ref. [31].

<sup>c</sup> The sum of  $\mu(\text{C}_6\text{H}_5\text{NO}_2) + \mu(\text{C}_6\text{H}_5\text{NH}_2)$  is 5.54 D quite in agreement with the experimental value of  $5 \pm 1$  D reported by Suslick et al. [15] for their related push–pull *meso*-tetraphenyl porphyrin with a push–pull system due to NH<sub>2</sub> and NO<sub>2</sub> groups.

<sup>d</sup> The calculated value of the related push–pull *meso*-tetraphenyl porphyrin synthesized by Suslick et al. [15] (see c) is 8.99 D, to be compared to the reported value of  $5 \pm 1$  D.

the donor group Y (see Fig. 1) on the opposite phenyl ring and also upon coordination of the Zn(II) ion.

### 3.3. EFISH and THG NLO responses

In order to avoid or minimize resonance enhancements of the NLO responses, EFISH measurements (Table 4) were carried out with a non-resonant incident wavelength of 1.907  $\mu\text{m}$ , whose second harmonic  $2\omega$  lies at 0.953  $\mu\text{m}$  in a transparent region of the absorption spectra of all the push–pull porphyrins and their metal complexes investigated, although the presence in this region of extremely weak d–d spin forbidden bands cannot be totally excluded for Cu(II) or Co(II) macrocycles [30]. However, resonance enhancements cannot be totally avoided in our THG measurements because the third harmonic  $3\omega$  occurs at 0.636  $\mu\text{m}$  quite close to

Table 4  
 $\gamma_{\text{EFISH}}$  and  $\gamma_{\text{THG}}$  measurements in  $\text{CHCl}_3$  solutions using an incident wavelength of 1.907  $\mu\text{m}$

Compound	$\gamma_{\text{EFISH}} (10^{-34} \text{ esu})^{\text{a}}$	$\gamma_{\text{THG}} (10^{-34} \text{ esu})^{\text{a}}$
H <sub>2</sub> A	(0.4)	(0.6)
H <sub>2</sub> B	$6 \pm 0.5$	$35 \pm 10$
PdB	$5.1 \pm 0.6$	$12 \pm 2$
H <sub>2</sub> C	$14 \pm 2$	$45 \pm 10$
PdC	$17 \pm 6$	$6 \pm 1$
H <sub>2</sub> D	$4.2 \pm 0.4$	$65 \pm 25$
CoD	$6 \pm 1.2$	$31 \pm 10$
NiD	$7 \pm 2$	$20 \pm 2$
PdD	$11 \pm 4$	$15 \pm 4$
PtD	$14 \pm 2$	$16 \pm 2$
CuD	$10 \pm 3$	$20 \pm 5$
ZnD	$8 \pm 1$	$22 \pm 7$
CdD	$13 \pm 4$	$55 \pm 30$

<sup>a</sup> Values in parenthesis are calculated by semiempirical MNDO–TDHF methods (see Section 2.3).

the region of  $Q$  absorption bands, particularly with free porphyrins H<sub>2</sub>B, H<sub>2</sub>C and H<sub>2</sub>D (Table 2). Evidence for resonance enhancements of the EFISH response was found for these free porphyrins by carrying out some measurements using also an incident wavelength of 1.34  $\mu\text{m}$ . In this latter case the second harmonic  $2\omega$  occurs at 0.670  $\mu\text{m}$ , close enough to the region of  $Q$  absorption bands of free porphyrins. We observed a significant increase of  $\gamma_{\text{EFISH}}$  by going from 1.907 to 1.34  $\mu\text{m}$ :  $\gamma_{\text{EFISH}}$  of H<sub>2</sub>B increases from  $6 \pm 0.5 \times 10^{-34}$  to  $45 \pm 10 \times 10^{-34}$  esu and that of H<sub>2</sub>D from  $4.2 \pm 0.4 \times 10^{-34}$  to  $14 \pm 2 \times 10^{-34}$  esu, as expected for strong or significant resonance enhancement originated by the strong  $Q$  absorption band at 0.647 and 0.650  $\mu\text{m}$ , respectively (Table 2).

In agreement with this origin of the resonance enhancement, when the porphyrin is coordinated to a 3d<sup>n</sup> metal,  $\gamma_{\text{EFISH}}$  values are not much affected by shifting the incident wavelength from 1.907 to 1.34  $\mu\text{m}$ :  $\gamma_{\text{EFISH}}$  of CuD moves from  $10 \pm 3 \times 10^{-34}$  to  $5 \pm 0.5 \times 10^{-34}$  esu and PdD from  $11 \pm 4 \times 10^{-34}$  to  $6.5 \pm 0.5 \times 10^{-34}$  esu. In these compounds, by complexation, any  $Q$  absorption bands above 0.600  $\mu\text{m}$  disappear so that the third harmonic cannot be too resonant (see Table 2).

We also found that the order of magnitude of  $\gamma_{\text{THG}}$  and  $\gamma_{\text{EFISH}}$  is similar ( $10^{-34}$  esu), as it was reported to occur in some asymmetrically substituted metal-free phthalocyanines [31]. Absolute  $\gamma_{\text{THG}}$  values in free porphyrins are always higher probably due, as already pointed out, to some resonance enhancement of  $3\omega$  (Table 4).

The comparable order of magnitude of  $\gamma_{\text{THG}}$  and  $\gamma_{\text{EFISH}}$ , as in the case of phthalocyanines [6], suggests a significant contribution to  $\gamma_{\text{EFISH}}$  of the electronic cubic term  $\gamma_0(-2\omega; \omega, \omega, 0)$  of Eq. (3):

$$\gamma_{\text{EFISH}} = \frac{\mu_0 \beta_{\text{vec}}(-2\omega; \omega, \omega)}{5 \text{ kT}} + \gamma_0(-2\omega; \omega, \omega, 0) \quad (3)$$

It follows that the usual approximation, used for classical push–pull organic systems in the evaluation of  $\beta_{\text{vec}}$  from  $\gamma_{\text{EFISH}}$ , neglecting the cubic term  $\gamma_0(-2\omega; \omega, \omega, 0)$  may give rise even in these porphyrins, as in other similar macrocycles [6,7], to  $\beta_{\text{vec}}$  values overestimated, particularly when they are basically low [15].

The not too different  $\gamma_{\text{EFISH}}$  values of H<sub>2</sub>D and its complexes with various 3d<sup>n</sup> metal ions ( $n = 7–10$ ) (Table 4) indicate also the absence of relevant effects on the  $\gamma_{\text{EFISH}}$  response upon coordination of the porphyrin to 3d<sup>n</sup> metal ion in contrast with the marked enhancement of the magnitude of the  $\gamma_{\text{EFISH}}$  response reported to occur upon coordination to some open shell 3d<sup>n</sup> metal ions of octasubstituted phthalocyanines [32].

However, in this latter case the enhancement of  $\gamma_{\text{EFISH}}$  by metal coordination was attributed to  $\omega$  resonance of the 1.064  $\mu\text{m}$  incident wavelength with



additional one-photon very weak forbidden d–d transitions of some 3d<sup>n</sup> metal ions, which could occur in the region 1.000–1.300  $\mu\text{m}$ . To a similar origin was attributed the dependence to metal coordination of  $\gamma(\omega; \omega, -\omega, \omega)$  response obtained by using Degenerate Four Wave Mixing (DFWM) for phthalocyanines and naphthocyanines coordinated to some open shell 3d<sup>n</sup> metal ions [33]. Obviously under our experimental conditions (incident wavelength at 1.907  $\mu\text{m}$ ) such a  $\omega$  resonance effect cannot occur.

### 3.4. Theoretical calculations of NLO responses

Theoretical calculations of the best geometries using the MNDO semiempirical approach [17], have confirmed that in porphyrins H<sub>2</sub>A, H<sub>2</sub>B, H<sub>2</sub>C and H<sub>2</sub>D and their Zn(II) complexes, the macrocycle is always essentially planar, while the aromatic rings in the meso position display, as expected, an arrangement nearly perpendicular to the macrocycle due to the repulsion of hydrogen atoms of the phenyl rings in the ortho position by the  $\beta$  hydrogen of the two adjacent pyrrolic rings [11,15]. This repulsion produces a torsional barrier about the C(meso)–C(aryl) bond [34], as confirmed by the X-ray crystallographic structure of H<sub>2</sub>A which shows a twisting between the phenyl rings and the plane of the porphyrin with an average dihedral angle of about 60° [35].

Differently from the ZINDO–SOS (sum over state) semiempirical approach proposed by Marks and co-workers [36], which is a time dependent perturbation method leading to a SOS [37], we used a semiempirical direct time dependent approach MNDO–TDHF, as proposed by Sekino and Bartlett [18b,23], and by Karna and Dupuis [18a], which allows the computation of the NLO responses without involving excited states (see Section 2.3). Recent theoretical studies on the NLO response of organic systems, using this approach, have been carried out based on ab initio methods (mainly Hartree-Fock and Density Functional Theory [38]), which are expected to give results more accurate than those based on semiempirical methods such as ZINDO or MNDO. However, ab initio methods can be carried out with reasonable computer time on relatively small (or periodic) molecular systems, particularly when using highly correlated methods. Up to now the systems investigated by ab initio methods are considerably smaller than those considered in the present study. Since our theoretical investigation was carried out only with the rather qualitative aim of confirming the experimental trends of  $\gamma_{\text{EFISH}}$  and  $\gamma_{\text{THG}}$  the approach based on the MNDO semiempirical method can give all the necessary informations. With this limitation in mind we found that the calculated order of magnitude of  $\gamma_{\text{EFISH}}$  values is in good agreement with the experimental one, whilst the order of magnitude of calculated  $\gamma_{\text{THG}}$  is always lower,

by one or two order of magnitude, than the experimental one (Table 5), producing additional evidence for relevant resonance contributions to experimental  $\gamma_{\text{THG}}$  values of free porphyrins and probably, although at minor extent, of their metal complexes. In fact our MNDO–TDHF approach does not take into consideration resonance effects.

Our calculations also confirm that the cubic electronic contribution  $\gamma_0(-2\omega; \omega, \omega, 0)$  to  $\gamma_{\text{EFISH}}$  response cannot be safely neglected at least in porphyrins with a relatively low second order NLO response as those investigated in this work. In fact in agreement with a small dipolar contribution  $\mu_0\beta_{\text{vec}}/5$  kT to  $\gamma_{\text{EFISH}}$  and with a more relevant contribution of  $\gamma_0(-2\omega; \omega, \omega, 0)$  measured  $\beta_{\text{vec}}$ , neglecting  $\gamma_0(-2\omega; \omega, \omega, 0)$ , is often negative while calculated  $\gamma_{\text{EFISH}}$  is positive (Table 5).

Still, in line with a significant contribution of  $\gamma_0(-2\omega; \omega, \omega, 0)$ , the calculated  $\gamma_{\text{EFISH}}$  for the rather symmetrical molecule H<sub>2</sub>A is similar, also as sign, to that of the more asymmetrical porphyrins H<sub>2</sub>B, H<sub>2</sub>C and H<sub>2</sub>D (Table 5), although for H<sub>2</sub>A the dipolar contribution  $\mu_0\beta_{\text{vec}}/5$  kT to  $\gamma_{\text{EFISH}}$  should be close to zero being the local symmetry  $D_{2h}$ . Calculations confirm also the limited role of metal coordination: coordination to Zn(II) of H<sub>2</sub>B, H<sub>2</sub>C and H<sub>2</sub>D produces only a small increase of both calculated  $\beta_0$  and  $\beta_{\text{vec}}$  (Table 5).

### 3.5. The order of magnitude of third order NLO properties from vibrational data

In the recent past it has been shown that when a strong electron–phonon coupling occurs [39,40] the vibrational hyperpolarizabilities can be extremely large. Therefore, at least the order of magnitude of both static second order  $\beta_0$  and third order  $\gamma_0$  responses could be evaluated from the contribution of the nuclear relaxation, in the hypothesis of an harmonic behaviour of both atomic vibrations and electron displacements [16] (see Section 2.4).

Table 5  
Calculated NLO parameters <sup>a,b</sup>

Compound	$\beta_0$ 10 <sup>–30</sup> (esu)	$\beta_{\text{vec}}$ 10 <sup>–30</sup> (esu)	$\gamma_{\text{EFISH}}$ 10 <sup>–34</sup> (esu)	$\gamma_{\text{THG}}$ 10 <sup>–34</sup> (esu)
H <sub>2</sub> A	–0.5	–6.5	0.4	0.6
ZnA	–4.3	–7.5	0.2	0.4
H <sub>2</sub> B	–2.5	–3.2	0.2 (6 $\pm$ 0.5)	0.7 (35 $\pm$ 10)
ZnB	9.7	16.1	1.9	0.4
H <sub>2</sub> C	–2.9	–3.8	0.1 (14 $\pm$ 2)	0.7 (45 $\pm$ 10)
ZnC	4.2	7.3	1.1	0.6
H <sub>2</sub> D	1.9	2.6	0.8 (4.2 $\pm$ 0.4)	0.6 (65 $\pm$ 25)
ZnD	5.7	9.1	1.3 (8 $\pm$ 1)	0.5 (22 $\pm$ 7)

<sup>a</sup> With the exception of  $\beta_0$ , all the values are referred to an incident wavelength of 1.907  $\mu\text{m}$ .

<sup>b</sup> Values under parenthesis are experimental values (Table 4).

This vibrational approach was applied with a certain success in the determinations of the static NLO properties of  $\pi$ -delocalised chain of organic systems such as polyenes, with or without polar end groups, or ribbon like molecules (rylenes) or even relatively smaller  $\pi$ -delocalised cyclic systems such as naphthalene, perylene and terylene [41].

Large static  $\beta_0$  values require simultaneous strong infrared and Raman intensities for the same normal mode (see Eq. (1)). Comparison of infrared and Raman spectra of  $\text{H}_2\text{D}$  (Fig. 3), shows that the strongest infrared bands have negligible Raman intensities and viceversa, as expected for a fundamentally centrosymmetric porphyrinic skeleton not too much perturbed by the push–pull asymmetrical substitution of the phenyl rings.

This trend is typical of all the push–pull porphyrins investigated in this work in agreement with their rather low second order NLO response. It was impossible to obtain a quantitative estimate of  $\beta_0$  because the measured absolute intensities of the few coincident infrared and Raman bands are within the experimental

error. Under the hypothesis that Hyper Raman intensities are negligible [42] their static cubic hyperpolarizability  $\gamma_0$  were evaluated, neglecting the first four terms of Eq. (2) (see Section 2.4), directly from measured Raman cross-sections. The  $\gamma_0$  values so determined are of the same order of magnitude of  $\gamma_0$  values calculated with our semiempirical MNDO–TDHF theoretical approach (Table 6), although they are much lower, also as order of magnitude, when compared to experimental  $\gamma_{\text{THG}}$  values measured with an incident wavelength of  $1.907\ \mu\text{m}$  (Table 4). This is an expected trend because these latter values are affected by strong resonance enhancements as experimentally and theoretically proved.

The most relevant contributions to  $\gamma_0$  originate from very low frequency vibrations (below  $400\ \text{cm}^{-1}$ ), which a careful spectroscopic work [43] assigned to skeletal modes of low frequency. Since in the evaluation of  $\gamma_0$  Raman intensities must be weighted by a factor  $1/\nu^2$  (see Eq. (1)), the contribution of the skeletal modes of low frequencies is very important even if their Raman intensities are not extremely strong.

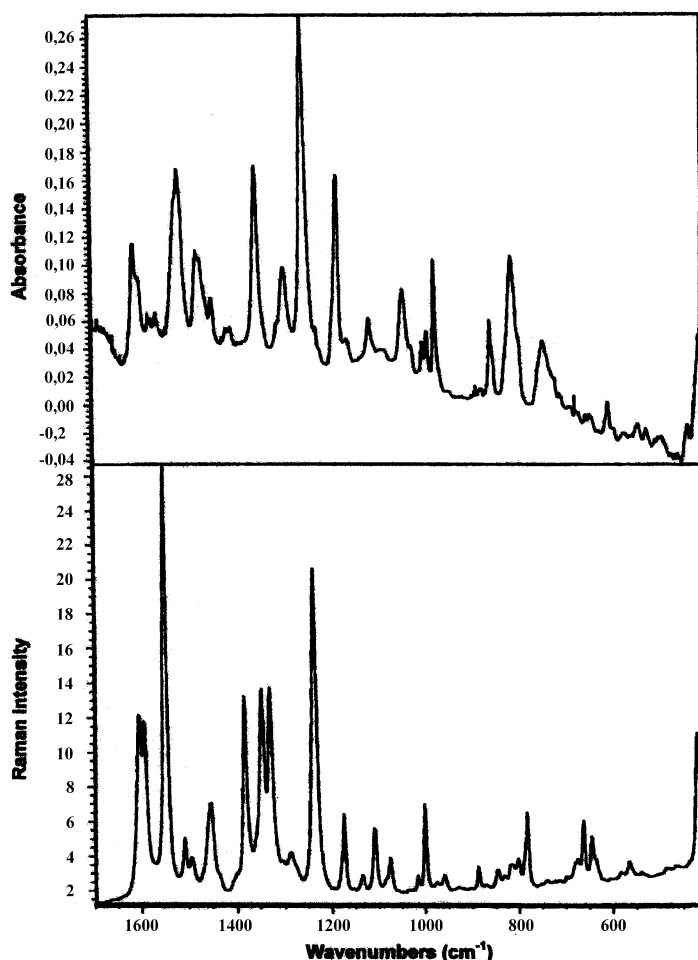


Fig. 3. Infrared (top) and Raman (bottom) spectra of  $\text{H}_2\text{D}$  in solid state.

Table 6  
 $\gamma_0$  values from Raman spectra

Compound	$\gamma_0 10^{-34}$ <sup>a</sup> (esu)	$\gamma_0 10^{-34}$ <sup>b</sup> (esu)	$\gamma_{\text{THG}} 10^{-34}$ <sup>c</sup> (esu)
H <sub>2</sub> D	0.99	2.54	65 ± 25
ZnD	0.67	1.7	22 ± 7
NiD	0.83	n.d.	20 ± 2
CuD	0.53	n.d.	20 ± 5

<sup>a</sup> Experimental from Raman spectra.

<sup>b</sup> Static value calculated with the MNDO–TDHF semiempirical method.

<sup>c</sup> Determined by THG experiments with 1.907  $\mu\text{m}$  incident wavelength.

#### 4. Conclusion

In this work we have confirmed, taking as reference asymmetrically substituted *meso*-tetraphenyl porphyrins, characterized by a limited  $\pi$  conjugation between the porphyrin and the aromatic rings and therefore by a limited second order NLO response [15] that, due only to the high polarizability of the  $\pi$ -delocalised porphyrin ring, the third order NLO response is substantial. It follows that their  $\beta_{\text{vec}}$  values, when low, obtained from  $\gamma_{\text{EFISH}}$  measurements could be affected by a significant overestimation because, as in asymmetrical phthalocyanines [31], the cubic contribution  $\gamma_0(-2\omega; \omega, \omega, 0)$  to  $\gamma_{\text{EFISH}}$  cannot be neglected. This warning was supported also by MNDO–TDHF calculations of both  $\gamma_{\text{EFISH}}$  and  $\beta_{\text{vec}}$ . In addition we have experimentally and theoretically confirmed that in porphyrins and in their metal complexes, showing strong absorption bands in the region 0.400–0.650  $\mu\text{m}$ , the second order NLO response [12], when working with an incident wavelength of 1.340  $\mu\text{m}$ , is affected by relevant resonance enhancements due to  $Q$  absorption bands. It follows that second order NLO responses of porphyrins and their metal complexes must be considered with some care particularly if these measurements have not been carried out working with a non-resonant incident wavelength of 1.907  $\mu\text{m}$ .

We also reached evidence that the coordination to a metal ion does not perturb much the  $\gamma_{\text{EFISH}}$  response, at least in the case of our porphyrins, when working with an incident wavelength of 1.907  $\mu\text{m}$ . This result is in contrast with what reported for other  $\pi$ -delocalised macrocycles such as octasubstituted phthalocyanines [32] or triazolohemiporphyrazines [7a], working with an incident wavelength of 1.064  $\mu\text{m}$ . But in these latter cases the increase of  $\gamma_{\text{EFISH}}$  by metal coordination to the  $\pi$ -delocalised macrocycle was attributed to a  $\omega$  resonance enhancement, due to some weak d–d absorption possibly occurring around 1.064  $\mu\text{m}$ .

MNDO–TDHF calculations have produced additional evidence for a relatively small effect on the second order NLO response upon coordination of our porphyrins to Zn(II). This irrelevant effect could be related to

the irrelevant effect of metal coordination on the Soret band [10]. Also with other porphyrins with a larger  $\pi$  conjugated push–pull system [12,13], it was reported that coordination of the porphyrin to Zn(II), Cu(II), Ni(II) does not produce significant effects on the Soret band [12,13]. Only when the macrocycle is originated by multichelation, which can introduce some rigidity of the organic skeleton and a totally new  $\pi$  electronic system on ligands such as flexible tetradentate asymmetrical Schiff bases, the effect of coordination to open shell 3d<sup>n</sup> metal ions in increasing the second order NLO response of the ligand is relevant and well established. As expected in these latter cases significant changes occur in the electronic absorption spectra upon coordination [44]. In conclusion our investigation has produced some evidence for a more careful evaluation of the experimental EFISH measurements of second order responses of porphyrins.

Finally, we have shown for the first time, although in a rather preliminary way, that a vibrational method [16] can give an acceptable evaluation of the order of magnitude of at least the static cubic hyperpolarizabilities  $\gamma_0$  of  $\pi$ -delocalised macrocycles and their metal complexes. With all its limitation this method, which is unaffected by resonance enhancements or by fluorescent contributions, could be in the future considered as the first choice for a facile and quick determination of the order of magnitude of the static second and third order NLO responses of  $\pi$ -delocalised macrocycles such as porphyrins and their metal complexes, which is the relevant issue for any technological applications.

#### Acknowledgements

This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Programma di Ricerca MURST di tipo interuniversitario nell'area delle scienze chimiche, ex 40%, 1997, Research title: Molecole per materiali funzionali nanostrutturati) and by Consiglio Nazionale delle Ricerche (Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate II, 1998, Research Title: Sintesi e sviluppo di composti molecolari organometallici e di coordinazione con proprietà ottiche non-lineari (NLO) e con proprietà elettriche anisotropiche e isotropiche). We thank Dr. Francesca Tessore, Dr. Elena Cariati and Dr. Silvia Bruni for some EFISH and THG measurements.

#### References

- [1] (a) D.S. Chemla, J. Zyss, *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol. I–II, Academic Press, Boston, 1987; (b) I. Ledoux, J. Zyss, in: I.C. Khoo, F. Simoni, C. Umeton

- (Eds.), *Novel Optical Materials and Applications*, John Wiley and Sons, New York, 1997, p. 1.
- [2] M. Blanchard-Desce, S.R. Marder, M. Barzoukas, in: D.N. Reinhoudt (Ed.), *Comprehensive Supramolecular Chemistry*, vol. 10 (and references therein), Pergamon Press, Oxford, 1996, p. 833.
- [3] D.R. Kanis, M.A. Ratner, T.J. Marks, *Chem. Rev.* 94 (1994) 195 (and references therein).
- [4] (a) J. Zyss, I. Ledoux, *Chem. Rev.* 94 (1994) 77;  
(b) J. Zyss, T. Chauvan, C. Dhenaut, I. Ledoux, *Chem. Phys.* 206 (1993) 409;  
(c) I. Ledoux, C. Dhenaut, I.D.W. Samuel, J. Zyss, *Nonlinear Opt.* 14 (1995) 23.
- [5] (a) N.J. Long, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 21 (and references therein);  
(b) H.S. Nalwa, *Appl. Organomet. Chem.* 5 (1991) 349;  
(c) D.M. Roundhill, J.P. Fackler, Jr., *Optoelectronic Properties of Inorganic Compounds*, Plenum Press, New York, 1999, p. 107.
- [6] (a) G. De la Torre, P. Vázquez, F. Agulló-López, T. Torres, *J. Mat. Chem.* 8 (1998) 1671 (and references therein);  
(b) G. De la Torre, T. Torres, F. Agulló-López, *Adv. Mat.* 9 (1997) 265.
- [7] (a) M.A. Diaz-Garcia, I. Ledoux, F. Fernández-Lázaro, A. Sastre, T. Torres, F. Agulló-López, J. Zyss, *J. Phys. Chem.* 98 (1994) 4495;  
(b) F. Fernández-Lázaro, T. Torres, B. Hanschel, M. Hanack, *Chem. Rev.* 98 (1998) 563 (and references therein).
- [8] J.S. Lindsey, in: F. Montanari, L. Casella (Eds.), *Metalloporphyrins Catalysed Oxidations* (and references therein), Kluwer Academic Publishers, Dordrecht, 1994, p. 49.
- [9] (a) D.V.G.L.N. Rao, F.J. Arauda, J.F. Roach, D.E. Remy, *Appl. Phys. Lett.* 58 (1991) 1241;  
(b) H.L. Anderson, S.J. Martui, D.D.C. Bradley, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 655;  
(c) S. Guha, K. Kang, P. Porter, J.F. Roach, D.E. Remy, F.J. Arauda, D.V.G.L.N. Rao, *Opt. Lett.* 17 (1992) 264;  
(d) K. Kandasauany, S.J. Shetty, P.N. Puntambekar, T.S. Srivastava, T. Kundu, S.P. Singh, *Chem. Commun.* (1997) 1159.
- [10] M. Gouterman, in: D. Dolphin (Ed.), *The Porphyrins*, vol. III, Academic Press, New York, 1978, p. 1.
- [11] I.D.L. Albert, T.J. Marks, M.A. Ratner, *Chem. Mater.* 10 (1998) 753.
- [12] S.M. LeCours, H.W. Guan, S.G. Di Magno, C.H. Wang, M.J. Therien, *J. Am. Chem. Soc.* 118 (1996) 1497.
- [13] L. Karki, F.W. Vance, J.T. Hupp, S.M. Le Cours, M.J. Therien, *J. Am. Chem. Soc.* 120 (1998) 2606.
- [14] M. Yeung, A.C.H. Ng, M.G.B. Drew, E. Vorpagel, E.M. Breitung, R.J. McMahon, D.K.P. Ng, *J. Org. Chem.* 63 (1998) 7143.
- [15] K.S. Suslick, C.T. Chen, G.R. Meredith, L.T. Cheng, *J. Am. Chem. Soc.* 114 (1992) 6928.
- [16] (a) C. Castiglioni, M. Gussoni, M. Del Zoppo, G. Zerbi, *Solid State Comm.* 82 (1992) 13;  
(b) M. Del Zoppo, C. Castiglioni, G. Zerbi, *Nonlinear Opt.* 9 (1995) 73.
- [17] M.J.S. Dewar, W. Thiel, *J. Am. Chem. Soc.* 99 (1977) 4899.
- [18] (a) S.P. Karna, M. Dupuis, *J. Comput. Chem.* 12 (1991) 487;  
(b) H. Sekino, R.J. Bartlett, *J. Chem. Phys.* 85 (1986) 976.
- [19] (a) I. Ledoux, J. Zyss, *Chem. Phys.* 73 (1982) 202;  
(b) D.J. Williams, *Angew. Chem., Int. Ed. Engl.* 23 (1984) 690 (and references therein).
- [20] (a) S.K. Saha, G.K. Wong, *Appl. Phys. Lett.* 34 (1979) 423;  
(b) B.F. Levine, C.G. Bethea, *Appl. Phys. Lett.* 24 (1974) 445.
- [21] E.A. Guggenheim, *Trans. Faraday Soc.* 45 (1949) 203.
- [22] A.D. Adler, F.R. Longo, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* 32 (1970) 2443.
- [23] H. Sekino, R. Bartlett, *J. Chem. Phys.* 94 (1991) 3665.
- [24] D. Kanis, M.A. Ratner, T.J. Marks, *J. Am. Chem. Soc.* 114 (1992) 10338.
- [25] J.J.P. Stewart, T.J. Seiler, *MOPAC Manual*, a program product, 6th ed., Research Laboratory, United States Air Force Academy, 1990.
- [26] J. Gorrat, I.M. Mills, *J. Chem. Phys.* 49 (1968) 1719.
- [27] M. Dupuis, A. Farazdel, S.P. Karna, S.A. Maluendes, HONDO-8, in: E. Clementi (Ed.), *Modern Techniques in Computational Chemistry MOTECC*, ESCOM, Leiden, 1990.
- [28] A. Willetts, J.E. Rice, D.M. Burland, D.P. Shelton, *J. Chem. Phys.* 97 (1992) 7590.
- [29] (a) J.S. Lindsey, I.C. Schreiman, H.C. Hsu, P.C. Kearney, A.M. Marguerette, *J. Org. Chem.* 52 (1987) 827;  
(b) C.H. Lee, J. Lindsey, *Tetrahedron* 39 (2000) 11427.
- [30] M.A. Diaz-Garcia, F. Agulló-López, A. Sastre, B. Del Rey, T. Torres, C. Dhenaut, I. Ledoux, J. Zyss, *Nonlinear Optics* 15 (1996) 251.
- [31] A.L. McLellan, *Table of Experimental Dipole Moments*, W.H. Freeman and Company, San Francisco, 1963, p. 1.
- [32] M.A. Diaz-Garcia, I. Ledoux, J.A. Duro, T. Torres, F. Agulló-López, J. Zyss, *J. Phys. Chem.* 98 (1994) 8761.
- [33] J.S. Shirk, J.R. Lindle, F.J. Bartoli, Z.H. Kafafi, A.W. Snow, M. Boyle, *Int. J. Opt. Phys.* 1 (1992) 699.
- [34] S.S. Eaton, D.M. Fishnild, G.R. Eaton, *J. Am. Chem. Soc.* 99 (1977) 6594.
- [35] S.J. Sliver, A. Tulinsky, *J. Am. Chem. Soc.* 89 (1967) 3331.
- [36] D.R. Kanis, P. Lacroix, M.A. Ratner, T.J. Marks, *J. Am. Chem. Soc.* 116 (1994) 10089 (and references therein).
- [37] B.J. Orr, J.F. Ward, *Mol. Phys.* 20 (1971) 513.
- [38] (a) B. Champagne, D.H. Mosley, J.G. Fripiat, J.M. Andre, *Adv. Quantum Chem.* 35 (1999) 95;  
(b) B. Kirtman, B. Champagne, D.M. Bishop, *J. Am. Chem. Soc.* 122 (2000) 8007;  
(c) B. Champagne, P. Fisher, A.D. Buckingham, *Chem. Phys. Lett.* 331 (2000) 83.
- [39] C. Castiglioni, M. Del Zoppo, P. Zuliani, G. Zerbi, *Synth. Met.* 71 (1995) 171.
- [40] P. Zuliani, M. Del Zoppo, C. Castiglioni, G. Zerbi, C. Andraud, T. Brotin, A. Collet, *J. Phys. Chem.* 99 (1995) 16242.
- [41] M.C. Rumi, G. Zerbi, K. Mullen, M. Rehal, *J. Chem. Phys.* 106 (1997) 24.
- [42] C. Castiglioni, M. Tommasini, M. Del Zoppo, *J. Mol. Struct.* 521 (2000) 137.
- [43] R.H. Felton, N.-T. Yu, in: D. Dolphin (Ed.), *The Porphyrins*, vol. III, Academic Press, New York, 1978, p. 347.
- [44] (a) S. Di Bella, I. Fragalà, I. Ledoux, M.A. Diaz-Garcia, T.J. Marks, *J. Am. Chem. Soc.* 119 (1997) 9550;  
(b) S. Di Bella, I. Fragalà, T.J. Marks, M.A. Ratner, *J. Am. Chem. Soc.* 118 (1996) 12747;  
(c) P.G. Lacroix, S. Di Bella, I. Ledoux, *Chem. Mater.* 8 (1996) 541.