Non-resonant third-order optical non-linearity of porphyrin derivatives

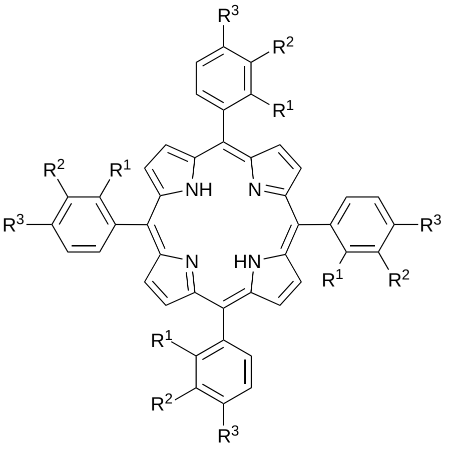
K. Kandasamy,[a] Shankar J. Shetty,[b] P. N. Puntambekar,[a] T. S. Srivastava,[b] T. Kundu[a] and Bhanu P. Singh*[a]

[a] *Department of Physics, Indian Institute of Technology, Bombay-400 076, India*
[b] *Department of Chemistry, Indian Institute of Technology, Bombay-400 076, India*

Non-resonant second molecular hyperpolarisabilities (γ) of tetraphenylporphyrin (H_2tpp) and five substituted derivatives are measured by the *Z*-scan technique at 784 nm; the relationship between the various structures and their corresponding molecular hyperpolarisabilities is explained on the basis of electronic interaction between the external substituents and the porphyrin core.

The non-linear optical properties of π-conjugated organic molecules[1,2] have been the subject of intense scientific research owing to their potential applications in photonic technology. Porphyrin derivatives are attractive owing to their large polarisable π-electron system. Further, these hold the promise of vast improvement in their optical non-linearities by way of molecular engineering. This requires an understanding of the structure–non-linearity relationship. Such an understanding is still in its infancy and more systematic studies are needed. With this motivation, we have undertaken the investigation of the effect of external substituents in porphyrin structures on their second molecular hyperpolarisabilities using the *Z*-scan technique.

Six porphyrin structures (Fig. 1) having external substitution of ester and methoxy groups at systematically varying positions of the phenyl ring have been synthesised using standard procedures.[3–5] Substituents were chosen such that their electron donating/accepting capacity varies. The third-order non-linear optical susceptibilities of 10^{-4} M solutions of these compounds in toluene were measured using the *Z*-scan[6] technique. A self-mode-locked Ti : sapphire laser, generating 60 fs transform limited pulses at 784 nm, was employed for these experiments. The laser beam was focused to a spot size of 25 μm using an 8 cm focal length lens and the 1 mm sample cell was scanned through its focal region. The experimental set-up was standardised by toluene. Its measured $\chi^{(3)}(-\omega,\omega,-\omega,\omega)$ value (4.55×10^{-13} esu) is in excellent agreement with the earlier reported value of 4.76×10^{-13} esu obtained by the optical Kerr effect.[7] The intensity levels in *Z*-scans of various samples varied in the range of 0.8–33.0 kW to contain the phase variation below π radians. For the measurement of non-resonant non-linearities, an excitation wavelength of 784 nm is chosen far away from the B (*ca*. 419 nm) and Q (*ca*. 615 nm) absorption bands of the porphyrins.



1 R^1 = H, R^2 = H, R^3 = H
2 R^1 = OCH_2CO_2Et, R^2 = H, R^3 = H
3 R^1 = H, R^2 = OCH_2CO_2Et, R^3 = H
4 R^1 = H, R^2 = H, R^3 = OCH_2CO_2Et
5 R^1 = H, R^2 = OCH_2CO_2Et, R^3 = OCH_2CO_2Et
6 R^1 = H, R^2 = OMe, R^3 = OCH_2CO_2Et

Fig. 1 Structures of porphyrins used in this study. 5,10,15,20-Tetraphenylporphyrin **1**, 5,10,15,20-tetrakis[2-(carboethoxymethyleneoxy)phenyl]porphyrin **2**, 5,10,15,20-tetrakis[3-(carboethoxymethyleneoxy)phenyl]porphyrin **3**, 5,10,15,20-tetrakis[4-(carboethoxymethyleneoxy)phenyl]porphyrin **4**, 5,10,15,20-tetrakis[3,4-bis(carboethoxymethyleneoxy)-phenyl]porphyrin **5**, 5,10,15,20-tetrakis[2-(carboethoxymethyleneoxy)-phenyl]porphyrin **6**.

A typical closed-aperture *Z*-scan for **2** is shown in Fig. 2. In all samples, it exhibits a pre-focal maximum followed by a post-focal minimum. This indicates a negative non-linear index of refraction. No transmittance variations in any of the open-aperture *Z*-scans are observed. This suggests that the measured non-linearities are predominantly refractive and non-resonant. Third-order non-linear susceptibilities $\chi^{(3)}$ for the solutions and the solvent were obtained by fitting the experimental *Z*-scan data to the expressions for the closed-aperture transmittance given in ref. 6. For a dilute solution of non-interacting particles, the second hyperpolarisability (γ) of the solute in a pairwise additive model,[8] is given by eqn. (1).

$$\gamma = \frac{\chi^{(3)}_{\mathrm{soln}} - \chi^{(3)}_{\mathrm{solvent}}}{L^4 N_{\mathrm{solute}}} \qquad (1)$$

where N_{solute} is the number density of solute, $L = (n^2 + 2)/3$ is the local-field factor[9] and n is the refractive index of the medium. The $\chi^{(3)}_{\mathrm{soln}}$ was found to vary linearly with concentration

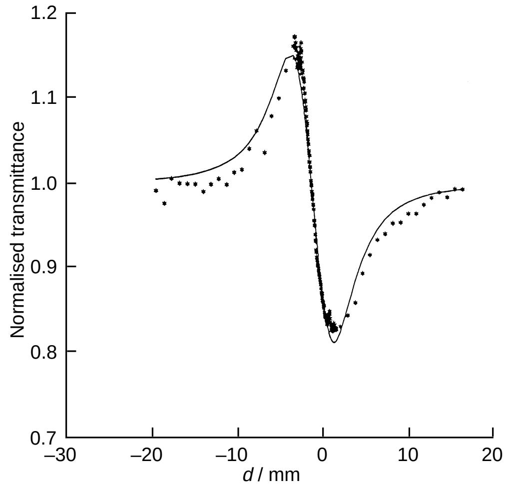


Fig. 2 Closed-aperture *Z*-scan trace of **2** in neutral conditions at 784 nm. The solid line represents the theoretical fit to eqn. (1).

for all the porphyrin derivatives. This justifies the applicability of pairwise additive model.

Table 1 shows the measured second molecular hyperpolarisabilities for six porphyrin derivatives. The influence of external substitution on the γ values is clearly evident. A very large enhancement of γ (nearly six times that of H_2tpp) is seen for **2** having ester groups at *ortho* positions. The external substituents can influence the γ values by perturbing the charge density in the porphyrin core. As a preliminary attempt to explain the systematics of the observed variation of γ with structural modification, the correlation was sought with the Hammett constant σ, a measure of substituents electron-donating/accepting capacity. The net Hammett constant[10] is given by

$$\sigma = Ca_r\sigma_r + a_i\sigma_i \qquad (2)$$

where a_r and a_i represent the relative contributions of resonant and inductive effects, and $C = 0.075$ for the *meta* position and unity otherwise. The values of the resonant (σ_r) and inductive (σ_i) parts of the Hammett constant for ester and methoxy groups are $\sigma_r = -0.4$, $\sigma_i = 0.33$ and $\sigma_r = -0.45$, $\sigma_i = 0.34$, respectively.

A linear relation between γ and σ is observed considering a 70% inductive and 30% resonant contribution. The inductive effect is expected to dominate as all these molecules in their free-base form have D_{2h} symmetry, since the porphine core and the phenyl ring are perpendicular to each other. Compound **2** has not been included in this correlation as the Hammett constant cannot be defined for substituents at the *ortho* positions. It is seen from Table 1 that a more positive value of σ results in reduced hyperpolarisability. The positive sign of σ indicates electron withdrawal from the core to the substituents. This leads to a decrease of the core electron density and hence a reduction of the hyperpolarisability.

To substantiate the above, the pH environment of porphyrin molecules was changed by adding a drop of trifluoroacetic acid to the samples. In the acidic environment, the symmetry changes from D_{2h} to D_{4h} owing to the formation of the dication[11] and a dramatic increase of the second hyperpolarisability was observed. A linear relation between γ and σ was observed when assuming a 70% resonant and 30% inductive effect. The resonant contribution is expected to dominate the interaction between the porphyrin core and the substituent, as for the D_{4h} symmetry, the core and the phenyl ring are almost parallel.[12] The calculated Hammett constants along with the observed hyperpolarisabilities are listed in Table 1. The negative sign of the Hammett constant implies an increase of the electron density in the core owing to electron donation by the substituents. It can be seen from Table 1 that the second molecular hyperpolarisability increases with increasing negative value of the Hammett constant. Thus, the observed trend of γ with the variation of substituent site is again consistent with our argument. The enhancement in the γ value of H_2tpp in an acidic environment over a neutral one may be attributed to increased π-electron delocalisation in the planar molecule, which is reflected in the red shift (*ca.* 20 nm) of the HOMO–LUMO gap in the absorption spectrum.

Table 1 Values of γ for six porphyrin derivatives in neutral and acidic environments. From repeated measurements and stability of the laser, the measurement tolerance is estimated to be ±2%

	Neutral		Acidic	
	$10^{30}\ \gamma$/esu	σ	$10^{30}\ \gamma$/esu	σ
2	−48.2	—	−273.5	—
1	−8.5	0.0	−20.7	0.0
4	−6.7	0.11	−31.0	−0.18
3	−6.5	0.22	−17.1	0.08
5	−6.3	0.33	−25.7	−0.10
6	−6.2	0.34	−25.4	−0.10

The important finding of this study is the massive enhancement of the non-linearity (*ca.* six times that of neutral H_2tpp) in **2** having substituents at *ortho* positions. An even larger non-linearity of this molecule (*ca.* 36 times that of neutral H_2tpp) is observed in an acidic environment. This high non-resonant non-linearity is large enough for practical non-linear optical devices.

In view of the arguments presented above, large enhancement of γ in **2** should arise due to (*i*) enhanced charge density in the core and (*ii*) increased π-electron delocalization.

Both of these effects will operate when the phenyl ring is not perpendicular to the core. The strong interaction between the β-pyrrole hydrogen and oxygen of the ester substituents at *ortho* positions may lead to increased planarity between the core and the phenyl ring.[13] The degree of planarity will depend upon the relative strength of the interaction between the β-pyrrole hydrogen and oxygen and steric hindrance due to the substituents. Substitution at *ortho* positions is expected to lead to more effective electron donation owing to its shear proximity to the core. In acidic conditions, further increased planarity in **2** will lead to still larger enhancement of the non-linearity for the above reasons.

In conclusion, non-linear properties of porphyrins can be vastly improved by external substitution of strong electron-donor groups at *ortho* positions of the planar porphyrin molecule. Further work to understand the origin of this enhancement at the microscopic level is in progress. However, this preliminary study provides some guidelines for molecular engineering.

We thank the Department of Science and Technology for financial support. Professor T. S. Srivastava would like to thank the All India Council of Technical Education for financial support.

Footnote

* E-mail: bhanups@niharika.phy.iitb.ernet.in

References

1 J. L. Bredas, C. Adant, P. Tackx and A. Persoons, *Chem. Rev.*, 1994, **94**, 243.

2 D. V. G. L. N. Rao, F. J. Aranda, J. F. Roach and David E. Remy, *Appl. Phys. Lett.*, 1991, **58**, 1241.

3 S. A. Syrbu, A. S. Semeikin, B. D. Berezin and O. I. Koifman, *Khim. Geterotsikl. Soedin*, 1989, **10**, 1373.

4 S. J. Shetty, S. Murugashan, S. R. Chatterjee, S. Banerjee, T. S. Srivastava, O. P. D. Noronha and A. M. Samuel, *J. Labelled Compd. Radiopharm.*, 1996, **38**, 411.

5 A. M. D'A Rocha Gonsalves, T. B. Varjao Jorge and M. M. Pereira, *J. Heterocycl. Chem.*, 1991, **28**, 635.

6 A. Sheik Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. Vanstryland, *IEEE J. Quantum Electron.*, 1990, **26**, 760.

7 P. P. Ho and R. R. Alfano, *Phys. Rev. A*, 1979, **20**, 2170.

8 Ming-Tang, B. P. Singh and P. N. Prasad, *J. Chem. Phys.*, 1988, **89**, 5535.

9 C. Sauturet, J. P. Hermann, R. Frey, F. Pradere, J. Ducuing, R. M. Baughman and R. R. Chance, *Phys. Rev. Lett.*, 1976, **36**, 956.

10 M. Meot-Ner and A. D. Adler, *J. Am. Chem. Soc.*, 1975, **97**, 5107.

11 M. Gouterman, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol III.

12 E. B. Fleischer, *Acc. Chem. Res.*, 1970, **3**, 105.

13 F. R. Longo, M. G. Finarelli and J. B. Kim, *J. Heterocycl. Chem.*, 1969, **6**, 927.

Received in Cambridge, UK, 26th March 1997; Com. 7/02098H