Metalloporphyrins for Quadratic Nonlinear Optics

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Cu^{II}- and Zn^{II}-based donor—acceptor porphyrins have been examined for second-order nonlinear optics using the hyper-Rayleigh scattering technique at 1064 nm. Introduction of the metal ions enhances the first hyperpolarizability (β) of the free-base donor—acceptor porphyrins significantly. The open shell Cu^{II} (d⁹) has a greater influence on β of these porphyrin systems than the closed shell Zn^{II} (d¹⁰). The high β values in the Zn^{II} porphyrins are understood in terms of the change in dipole moments upon excitation within the context of the two-state model as well as two-photon resonance enhancement. In Cu^{II} porphyrin complexes a large number of excited states seem to contribute to β with, perhaps, a little contribution from two-photon resonance at the excitation wavelength.

Introduction

There has been an increasing interest in the search for new nonlinear optical (NLO) materials that are transition metal organometallics and coordination complexes^{1,2} exhibiting large microscopic (β) and macroscopic (χ^2) second-order nonlinearities. Extensively delocalized cyclic π -systems, such as phthalocyanines and porphyrins, are studied as third-order NLO materials^{3,4} owing to their symmetric structures in nature. Second-order NLO properties, which are exploited in telecommunication, data storage, and information-processing applications, arise in molecules that lack a center of symmetry. The meso-tetraphenylporphyrins (TPP) are highly soluble in a variety of solvents and exhibit interesting optical characteristics. In addition, structural modification of TPP can easily be brought about by varying the central metal ion and/or substitution of organic donor-acceptor (D-A) moieties, thereby providing a two-dimensional network for effective intramolecular charge transfer (ICT). An appropriate tuning of porphyrin structures may result in a large second harmonic response. The electricfield-induced second harmonic (EFISH) generation measurements of unsymmetrically substituted aminonitrotetraphenyl free-base porphyrins reported by Suslick et al.⁵ have shown that the first hyperpolarizability of these molecules are lower ($\beta =$ $(10-30) \times 10^{-30}$ esu) than what is expected a priori for such large cyclic π -systems. The lower β values are due to the cancellation of CT interactions in the parallel and perpendicular directions of the permanent dipole moment along which the major component of β is measured in the EFISH experiments. Unfavorable orientation of the meso aryl groups (bearing the amino and nitro substituents) with reference to the porphyrin plane also reduces the CT interactions between the push-pull groups in the above examples.

In this paper, we describe a new class of functionalized fluoroaryl porphyrins bearing nitro- (situated at the 2-position in a pyrrole ring) and *N*,*N*-dimethylamino groups (the para position of each of the aryl group) in the vicinity of the cyclic π -system (Figure 1), which exhibits moderate second-order nonlinearity. To understand the effect of metal ions on the NLO response, zinc(II) and copper(II) derivatives of the synthesized porphyrins were also investigated in this paper. We have employed the hyper-Rayleigh scattering (HRS) technique for



Figure 1. Structures of the donor-acceptor porphyrins.

the determination of the average hyperpolarizability $\langle\langle\beta\rangle\rangle$ in solution.^{6–9} Semiclassical results on the dynamic first hyperpolarizability of the free-base porphyrins in the gas phase are contrasted with the experimental values.

Experimental Section

The pentafluorophenyl porphyrin has been synthesized through the conventional route.¹⁰ The nitration of one of the pyrrole carbons has been accomplished by nitration of Cu**a** (see Figure 1) with Cu(NO₃)₂ in CHCl₃ followed by a demetallation reaction. The amination at the para position of the *meso*fluorophenyl rings of the unsubstituted porphyrin was achieved by refluxing corresponding porphyrins with dimethylamine hydrochloride in DMF. A modified procedure was followed for the amination of the phenyl rings of the nitro-substituted porphyrins.¹¹ The corresponding metal derivatives were prepared using metal(II) acetates as metal carriers. Compounds were characterized by UV–visible, ¹H-NMR, ¹⁹F-NMR, and FAB-MS spectroscopies.

The experimental setup for the hyper-Rayleigh scattering technique has been described in detail elsewhere.^{9,12} Briefly, the fundamental from a Nd:YAG laser (Spectra Physics, 8ns,

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Figure 2. Quadratic coefficient $I_{2\omega}/I_{\omega}^2$ vs number density of compound **d** in dichloroethane solution.

<10 mJ/pulse) is focused tightly on a glass cell containing the solution of the compound. The two-photon Rayleigh scattering signal is imaged efficiently in the perpendicular direction onto a visible sensitive photomultiplier tube. A 3 nm bandwidth 532 nm interference filter is used on the signal path to isolate the second-harmonic light. Finally, the signal is averaged and recorded. The laser power is kept low to avoid stimulated Raman and Brillouin scattering and other nonlinear processes. The theory of the harmonic light scattering has been developed by several authors.^{6,7,13} For a mixture of two different species, e.g., for a solute and a solvent, the resulting second-harmonic intensity $I_{2\omega}$ is related to the incident laser intensity, I_{ω} in the following way:

$$I_{2\omega} = G(N_{\text{solvent}}\beta^2_{\text{solvent}} + N_{\text{solute}}\beta^2_{\text{solute}})I_{\omega}^2$$
(1)

where *G* is an instrument factor, N_i is the number density of the *i*th species in solution, and β_i is the first hyperpolarizability. Terhune *et al.*⁶ calibrated carbon tetrachloride with respect to quartz, using the same HRS technique, and we have calibrated dichloroethane by a method similar to that described by Zyss *et al.*⁸ and obtained $\langle \beta_{dichloroethane} \rangle = 0.42 \times 10^{-30}$ esu. Equation 1 is adequate for the solutes that do not absorb significantly at ω or 2ω . However, compounds investigated here absorb in the green (2ω), and corrections as suggested by Clays *et al.*⁷ are necessary in these cases. The modified equation, which can take into account the absorption at the second-harmonic frequency, can be expressed as

$$I_{2\omega} = (N_{\text{solvent}}\beta_{\text{solvent}}^2 + N_{\text{solute}}\beta_{\text{solute}}^2)I_{\omega}^2 10^{-\epsilon(2\omega)cl}$$
(2)

where $\epsilon(2\omega)$ is the absorption cross section (in cm²) of the solute at the second-harmonic frequency, and *l* (in cm) is the effective path length. Figure 2 shows the $I_{2\omega}/I_{\omega}^2$ vs number density plot for compound **d**. The nonlinear nature of Figure 2 at high concentrations of the solute is due to the self-absorption of the porphyrin at 532 nm. The slope and intercept of the plot at low concentrations (the linear part of Figure 2) permit evaluation of β values. Since protonation and deprotonation of the TPP free base is possible, we checked for the presence of charged species, which, in principle, can affect the β -values in solution.^{9,14} We found that (data not shown) at neutal pH, that is, under the conditions of the experiments, the extent of protonation or deprotonation is negligible (<0.1%). Therefore, we assume that the molecules exist as neutral species in solution and the measured hyperpolarizability value is attributed to that

TABLE 1: Experimental β 's (×10³⁰) in esu,^{*a*} Calculated Dipole Moments (μ_g) in Debye (D), Calculated β 's (×10³⁰) in esu, and Extinction Coefficients, ϵ (×10⁻³) in mol⁻¹ cm⁻¹ at 532 nm for All the Compounds

compounds	$\beta_{ m HRS}$	β	$\mu_{ m g}$	ϵ
а	1.90	1.20	1.33	2.37
b	7.20	3.20	1.27	4.79
с	10.1	4.60	6.12	6.25
d	54.0	32.0	9.78	12.7
Zna	2.80			11.3
Znb	11.2			11.0
Znc	11.8			3.42
Znd	92.0			5.82
Cua	3.90			15.9
Cub	19.2			18.3
Cuc	19.6			8.61
Cu d	118			9.54

^{*a*} The error is within $\pm 7\%$.

of the neutral species. All the absorption spectra were recorded in a Hitachi (U-3400) spectrophotometer at room temperature.

Results and Discussions

First hyperpolarizabilities of the metalloporphyrins and the corresponding free-base porphyrins obtained by the HRS technique at 1064 nm in dichloroethane ($\beta = 0.42 \times 10^{-30}$ esu) are listed in Table 1. Gas phase first hyperpolarizabilities (β) of the free-base porphyrins are computed using the intermediate neglect of differential overlap package of Zerner employing the correction vector (ZINDO/CV)15 technique. We employed molecular mechanics (MMX) optimized structures as input geometries and an excitation energy of 1.17 eV, same as the experimental photon energy at 1064 nm, for β calculations. In the ZINDO/CV calculations we have retained all singly and doubly excited configurations generated from the ground state Slater determinant by considering 10 HOMOs and 10 LUMOs. Calculated dipole moments and β 's for the free-base porphyrins are given in Table 1. The trend in the experimental β values is reproduced satisfactorily in the calculation. Nonzero dipole moment and β for symmetrically substituted porphyrin such as **a** indicate that the phenyl rings are not in the same plane with the porphyrin ring. The β values are found to be highly sensitive to the nature and position of the substituents. In the free-base porphyrins, this value increases 3.5 times with the amino substituent on each of the meso-phenyl rings (total of four donor groups), while it increases by a factor of 5 in the nitro-substituted porphyrin. In the amino porphyrins, four amino groups are positioned at the para position of each meso aryl ring disposed about 70° to the mean porphyrin plane.¹⁶ This would enforce steric constraints for direct interaction of the phenyl rings with macrocyclic π -pathways, which hinders effective charge transfer resulting in a β value less than expected for such a large system. In this regard, the nitro group at one of the pyrrole carbons in **c** is in the conjugative pathway and β is higher than **b** in spite of the combination of four strong donor N,N-dimethylamino groups in the latter. The effectiveness of the CT interaction between the nitro (acceptor) group and the porphyrin (donor) moiety in c is also evident from a calculated high ground state dipole moment as well as high β of this molecule. The highest value of β was obtained when both N,N dimethylamino and nitro groups are present in the porphyrin moiety as in d. This is understandable, since their presence within the porphyrin periphery reinforces ICT as revealed from the results of ground state dipole moment calculations. The ground state of **d** is more polarized than the other free-base derivatives. It may be noted here that although the porphyrin ring is highly conjugated, the measured β values are lower than those reported for the same D–A acyclic trienes (only three double bonds between the donor and the acceptor).^{17,18} A possible reason for this lies in the cyclic π -conjugation that normally reduces the effective path length for π -electron delocalization. For example, cyclic triand tetraene systems always have lower β values compared to their acyclic analogues with the same donor–acceptor substitutions. Charge transfer interaction between the donor and acceptor through a π -electron backbone is most favorable when the double bonds are in an all-*trans* configuration.¹⁹

In these free-base porphyrins, β increases substantially on metallation. The presence of metal ions eliminates the distinct CT interaction arising from the nitro or dimethylamino substitution (compounds b, c, vs Znb, Znc and Cub, Cuc). The major effect due to the metal ion is observed in the derivatives bearing both donor and acceptor moieties. Solvatochromic studies on both absorption and fluorescence transitions of all the compounds (data not shown) indicate that with increasing solvent polarity both bands shift to the red region. This suggests that the change in dipole moment, μ , is positive, and within the context of the two-state model, $\frac{20}{\beta}$ is also positive. We have observed from the solvatochromic measurements that μ is higher for compound Znd than either amino- or nitro-substituted porphyrins (Znb and Znc). Also, significant solvatochromic shifts of the emission bands were observed in the case of Znd $(\lambda_{ex} = 410 \text{ nm})$ compared to that in **d**, indicating more chargetransfer nature of the excited state of the zinc(II) derivative than the corresponding free-base porphyrin. Therefore, the higher value of β in the Zn^{II} derivatives originates partly in the large change in dipole moment upon excitation. However, the absorption shifts in Cu^{II} complexes in various solvents are not significant, implying that the two-state model cannot account for the high β values in Cu^{II} porphyrins. It is of interest to note that for the same D-A substituents, the open shell metal ion Cu^{II} (d⁹ system) exhibits (Table 1) a higher β value than the corresponding closed shell Zn^{II} (d¹⁰ system) porphyrin. Similar observations have been made recently by Di Bella et $al.^{21}$ for a series of metallosalophen systems. They have shown experimentally as well as theoretically by the ZINDO/sum-overstate (SOS) approach that for the same ligand, open shell metal ions [Cu^{II} and Co^{II} in their case] lead to much higher β values than the closed shell Ni^{II} metal ion. Unlike in the Cu^{II}-salophen complexes, we have not observed any distinct metal-ligand or ligand-metal charge transfer band (MLCT or LMCT) in the visible or near-UV region of the absorption spectrum for open shell CuII porphyrins. Since all the porphyrin molecules studied here absorb 532 nm light ($\epsilon_{532} \ge 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), the two-photon resonance enhancement of β will be significant.²² For similar substitutions, ϵ_{532} values of copper(II) derivatives are higher than those of the zinc(II) derivatives. Therefore, two-photon resonance enhancement is partially responsible for the large β in Cu^{II} porphyrins. However, the free-base porphyrin **d**, which has the highest ϵ_{532} value relative to the corresponding copper-(II) and zinc(II) derivatives, exhibits the lowest β value among them. Therefore, we believe that the contribution from resonance enhancement to the first hyperpolarizability cannot be all that important and the metal d-electrons are more effective in fine tuning the first hyperpolarizability.

Conclusion

In this paper, we report a series of metalloporphyrins specifically tailored for quadratic NLO properties. The molecular hyperpolarizabilities of these porphyrins are high, but the cyclic nature of the π -backbone and dihedral twist of the phenyl rings with respect to the porphyrin base limit highly efficient coupling of donor acceptor moieties across the porphyrin periphery. The β values of Zn^{II} porphyrins can be adequately accounted for by invoking the two-state model. For the Cu^{II} porphyrin derivatives, however, the origin of nonlinearity is very much different and the contribution to β from other electronic states seems to be responsible for large β values. Work is in progress to further probe the role of the metal ion electronic configuration on the NLO response of metalloporphyrins as well as the effect of solvent polarity on their β values.

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