Electronic Stark Effect Studies of a Porphyrin-Based Push−Pull Chromophore Displaying a Large First Hyperpolarizability: State-Specific Contributions to β

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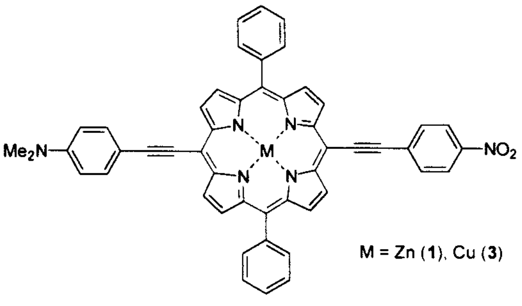
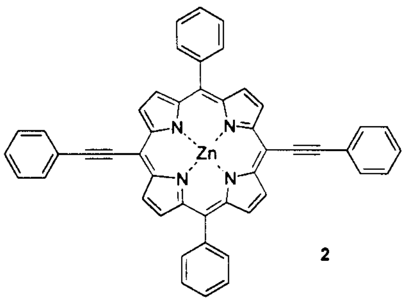
Abstract: Electroabsorption or Stark effect spectroscopy has been applied to a pair of porphyrin-based chromophores with the aim of deriving a detailed understanding of the origin of the remarkable first hyperpolarizability, β, of one of the chromophores: [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)-ethynyl]-10,20-diphenylporphinato]zinc(II). The measurements show that significant changes in molecular dipole moment, $\Delta\mu$, accompany excitations of x-polarized transitions of the aminophenyl (donor)/nitrophenyl (acceptor) functionalized chromophore, but are absent for a related chromophore lacking the donor and acceptor groups. For linear chromophores, changes in dipole moment are a prerequisite to effective molecular first hyperpolarization and incident light frequency doubling behavior. A more detailed consideration of the available $|\Delta\mu|$ data, within the context of a conventional two-level model, has yielded the following: (a) specific information about the roles of each of seven electronic and vibronic excited states in defining β, (b) a semiquantitative explanation for the apparent frequency independence of β found in previous hyper-Rayleigh scattering experiments performed at 830 and 1064 nm, and (c) an explanation for the contrasting frequency dependence of the nonlinear optical response for the analogous Cu(II)-containing chromophore. Finally, the experimental findings are in generally good agreement with published ZINDO calculations which had pointed toward the exceptional effectiveness of yne linkages in coupling donor and acceptor moieties to the highly polarizable porphyrin core assembly.

Introduction



M = Zn (**1**), Cu (**3**)



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Recent reports have described the synthesis and remarkable spectroscopic properties of the first few members of a new family of chromophores that feature electron-releasing and electron-withdrawing groups fused via an intervening ethynyl moiety to the carbon framework of a porphyrin macrocycle.[1] Particularly striking are the large molecular first hyperpolarizabilities (β) exhibited by electronically asymmetric, donor−acceptor (D−A) versions of this new structural motif, exemplified in particular by [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphinato]-zinc(II), **1**. High dilution hyper-Rayleigh measurements in chloroform solvent show that the first hyperpolarizability (i) exceeds 5000×10^{-30} esu when this compound is evaluated with 830 nm excitation and (ii) remains unchanged (within experimental error) when the wavelength of incident light is extended to 1064 nm.[2] ZINDO based sum-over-states calculations of two- and three-level effects provide some insight into the origin of the large β(830) and β(1064) values.[3] In particular, they point to the importance of ground-state/excited-state dipole moment changes ($\Delta\mu$) that accompany strongly allowed transitions. They also point to the role played by the porphyrin-localized orbitals, which facilitate substantial donor−acceptor electronic coupling.[1,3] They do not account, however, for the apparent independence of β over the 830-to-1064 nm wavelength domain.[3] We reasoned that corroborative and/or complementary insight could be gained by experimentally evaluating

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(1) (a) LeCours, S. M.; Guan, H. W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497. (b) LeCours, S. M.; DiMagno, S. G.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 11854.

$|\Delta\mu|$ for key transitions. We report here on the dipole moment changes accompanying the seven lowest energy electronic transitions defining the B- and Q-band absorption envelopes and use this information in a two-level formulation to (a) delineate state-specific contributions to β, (b) rationalize the approximate frequency independence of β for the zinc-containing chromophore, and (c) understand the origin of the frequency *dependent* behavior of β for the corresponding (porphinato)-copper(II) complex.[1]

Experimental Section

To obtain dipole moment changes, we made use of low-temperature electroabsorption spectroscopy (electronic Stark effect or electric field effect spectroscopy). The experimental procedure and the data reduction method have been described in detail elsewhere.[4] Briefly, however, electroabsorption experiments were performed at 77 K in a 2-methyltetrahydrofuran glass by using a retrofitted and computer-controlled Cary-14 spectrophotometer in a single beam mode. The electroabsorption cell (indium tin oxide coated quartz plates; Kapton tape spacers) was 50 μm thick, as determined interferometrically in the near-infrared region with an empty cell. The field-dependent and independent transmittance signals were detected by a photomultiplier tube (Hamamatsu R928; near-UV and blue region) and a silicon photodiode (Hamamatsu S5591; red and near-infrared region). After passage through a current-to-voltage converter, the small second-order Stark transmittance signal ($V_{2\omega}$) was detected with a digital lock-in amplifier (Stanford Research, SR 850) at the second harmonic of the field modulation frequency (ω; typically 220 Hz).

According to Liptay, for a rigid, isotropic sample the wavelength-dependent change in absorption as a function of electric field, $\Delta A(\nu)$, is given by a linear combination of zeroth, first, and second derivatives of $A(\nu)$:[5]

$$\Delta A(\nu) = \left\{ A_x A(\nu) + \frac{B_x}{15hc}\frac{\nu \mathrm{d}[A(\nu)/\nu]}{\mathrm{d}\nu} + \frac{C_x}{30h^2c^2}\frac{\nu \mathrm{d}^2[A(\nu)/\nu]}{\mathrm{d}\nu^2} \right\} \cdot F_{\mathrm{int}}^{\;2} \qquad (1)$$

where h is the Planck's constant, c is the speed of light, ν is the energy in wavenumbers, and F_{int} is the internal field experienced by the molecules.[6] The coefficients A_x, B_x, and C_x have been described in detail elsewhere.[7] Briefly, C_x gives information regarding $|\Delta\mu_{12}|$, B_x gives information regarding the polarizability change, $\Delta\alpha_{12}$, and a cross term involving the transition moment polarizability and dipole moment, and A_x provides information about the changes in the transition moment polarizability and hyperpolarizability.

Results and Discussion

Absorption and Electroabsorption Spectroscopy. Figure 1A shows a visible and near-infrared absorption spectrum for **1** at 77 K in a 2-methyltetrahydrofuran glass. In this environment, the normally overlapping electronic transitions in both the Soret (B) and Q-band regions are reasonably well resolved with respect to the ambient temperature spectrum.[1] The lowest energy band ($E_{\mathrm{op}} = 14\,300$ cm^{-1}) is assigned as $Q_x(0,0)$, i.e., excitation to the lowest singlet excited state where x denotes polarization along the donor/acceptor axis (y is then perpendicular to x in the plane of the molecule and z is out of the plane of the molecule).[1,8] The shoulder at slightly higher energy is tentatively assigned as the corresponding y-polarized transition, while the relatively weak, broad band at 15 500 cm^{-1} is assigned as the first overtone of the Q_x and/or Q_y transition.[1] The bands at 19 400 and 20 700 cm^{-1} are assigned as $B_x(0,0)$ and $B_x(1,0)$ transitions while those occurring at 21 800 and 23 300 cm^{-1} are assigned as their y-polarized counterparts (see below). The dotted lines in Figure 1A correspond to a Gaussian deconvolution of the spectrum. Note that the dashed line, corresponding to the sum of the Gaussians, successfully reproduces the experimental spectrum.

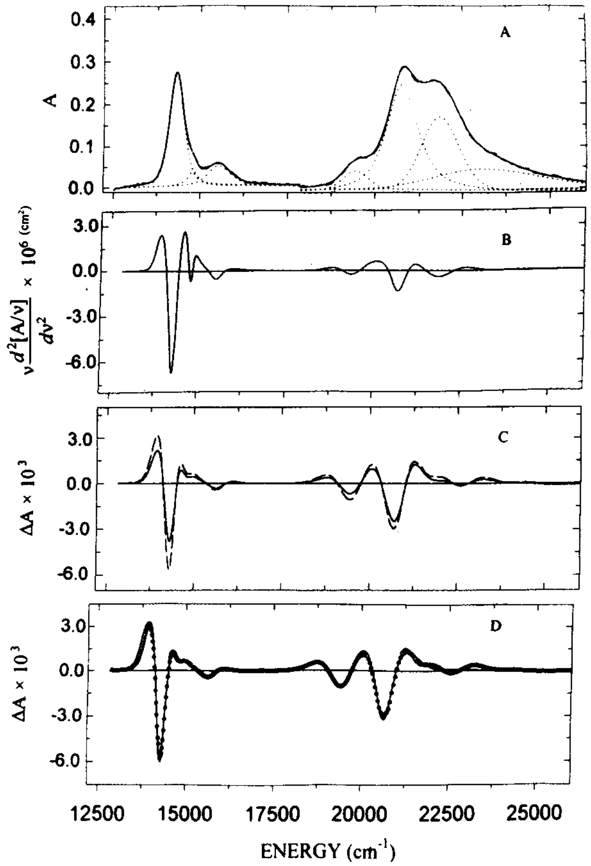

Figure 1. Panel A: Absorption spectrum of **1** in 2-mTHF glass at 77 K. Dotted lines show the fitted components of the absorption bands. Panel B: Second derivative of the overall absorption band. Panel C: Electroabsorption response at $\chi = 90°$ (solid line) and 55° (dashed line). Panel D: Measured (circles) and fit (eq 1; solid line) electroabsorption spectra at 55°.

Figures 1B shows the numerical second derivative of the absorption band. Figure 1C displays the experimental electroabsorption signal at angles, χ, of 55° and 90° between the applied electric field and the polarized optical excitation beam. As expected from eq 1, the electroabsorption response is quadratic in the applied electric field, with no new features

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[2] For reference, the reported wavelength-dependent hyperpolarizabilities, $\beta(\lambda)$ of a few reported chromophores are the following: (a) DANS: $\beta(1907\ \mathrm{nm}) = 73 \times 10^{-30}$ esu (Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103); (b) meso substituted donor/acceptor porhyrins: $\beta(1907\ \mathrm{nm}) \approx 30 \times 10^{-30}$ esu (Suslick, K. S.; Chen, C. T.; Meredith, G. R.; Cheng, L.-T. *J. Am. Chem. Soc.* **1992**, *114*, 6928); (c) (julolidinyl)$-$(CH=CH)$_3$$-$CH=(*N,N'*-diethylthiobarbituric acid): $\beta(1907\ \mathrm{nm}) = 2169 \times 10^{-30}$ esu (Marder, S. R.; Cheng, L.-T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skinhøj, J. *Science* **1994**, *263*, 511).

[3] Priyadarshy, S.; Therien, M. J.; Beratan, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 1504.

[4] (a) Karki, L.; Lu, H. P.; Hupp, J. T. *J. Phys. Chem.* **1996**, *100*, 15637. (b) Karki, L.; Hupp, J. T. *Inorg. Chem.* **1997**, *36*, 3318.

[5] Liptay, W. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1974; Vol. 1, pp 129$-$229.

[6] The internal field is the product of the externally applied local field correction factor. For a spherical cavity model, the correction factor (assuming a solvent continuum) is $3\epsilon/(2\epsilon + 1)$. The experimentally determined value of ϵ for 2-methyltetrahydrofuran glass is 4.0, which yields an estimated correction factor of 1.28.

[7] (a) Boxer, S. G. In *The Photosynthetic Reaction Center*; Academic Press: New York, 1993; Vol. II, pp 179$-$220. (b) Stefan, M. A.; Lao, K.; Boxer, S. G. *Science* **1994**, *264*, 810.

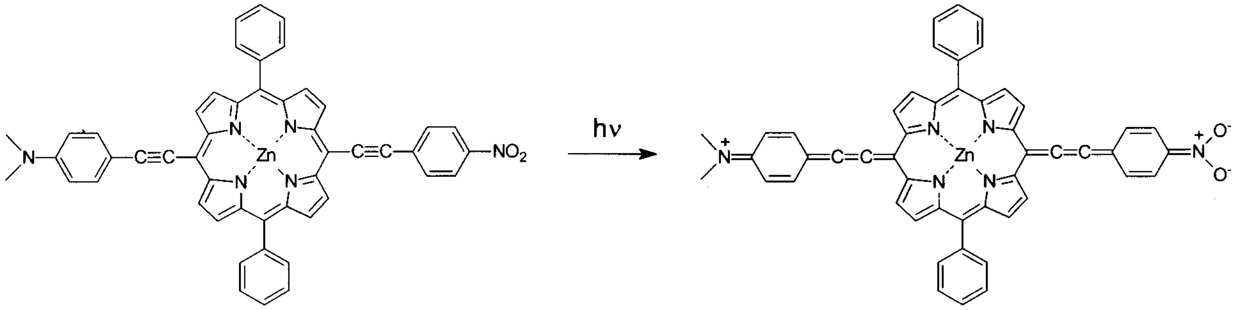
[8] (a) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105. (b) Kalyansundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1992.

Table 1. Calculated and Experimental Optical and Electronic Parameters for **1**

porphyrin transition	E_{op} (cm^{-1})	calcd $\Delta\mu_{12}$[a] (D)	exp $\lvert\Delta\mu_{12}\rvert$ (D)	P_{12}[b] (D)	β'_0[c] (10^{-30} esu)	$\beta'(1907)$[c] (10^{-30} esu)	$\beta'(1064)$[c] (10^{-30} esu)	$\beta'(830)$[c] (10^{-30} esu)
$Q_x(0,0)$	14 300	1	9 ± 1	3.4 ± 0.7	80	190	−190	−140
$Q_y(0,0)$	15 100	0	0[d]	1.1 ± 0.2	0	0	0	0
$Q_x(1,0)$	15 500	1	8 ± 1	1.7 ± 0.3	15	30	−50	−30
$B_x(0,0)$	19 400	16	15 ± 2	2.2 ± 0.5	30	40	630	−90
$B_x(1,0)$	20 700	10	13 ± 2	5.8 ± 0.5	160	220	1100	−660
$B_y(0,0)$	21 800	0	5 ± 3	5.4 ± 0.5	50	60	220	−300
$B_y(1,0)$	23 200	0	0 ± 2	4.1 ± 0.5	0	0	0	0
sum					335	540	1710	−1220

[a] ZINDO estimates by Prof. David Beratan and Dr. Satyam Pridarshy. [b] Transition dipole moments were derived from oscillator strengths measured at 77 K (see ref 11). [c] Values derived from eq 2 and experimental absorption and electroabsorption data. [d] No signal detected.

Scheme 1



appearing as the field strength is increased to its maximal value (5×10^7 V/m; see Supporting Information). From a comparison of spectra B and C in Figure 1 it is clear that the overall line shape is dominated by second-derivative contributions, implying that significant changes in dipole moment accompany optical excitation. Note, however, that little Stark activity accompanies the lower energy Q_y and the higher energy B_y transitions, consistent with their assignment as *y*-polarized transitions whose transition moment vectors are perpendicular to the donor (D) and acceptor (A) axis.

Figure 1D compares the experimental electroabsorption spectrum at 55° with fits to eq 1, where fitting in the Q and B regions was done independently. A six-parameter fit for the Q-bands (two absorption bands) yielded absolute $\Delta\mu_{12}$ values of 9 ± 1 and 8 ± 1 D for the $Q_x(0,0)$ and $Q_x(1,0)$ transitions, respectively; the $Q_y(0,0)$ transition is Stark silent.[9,10] In the B band region large dipole moment changes were found for the *x*-polarized transitions, but negligible changes were observed for the *y*-polarized transitions (Table 1). These findings imply that D−A functionalization of the porphyrin framework using cylindrically π-symmetric linkages at the porphyrin 5- and 15-positions imparts substantial charge transfer character to these low-lying, predominantly porphyrin-localized electronic transitions that are polarized along the D−A axis.[12] Because visible/near-IR optical excitation of such chromophores leads to enhanced electronic communication between the porphyrin-pendant D−A moieties, electronically excited **1** can be considered to possess partial cumulenic character (Scheme 1).[1,13−14]

Figure 2 shows the results of a control experiment involving [5,15-bis[(phenyl)ethynyl]-10,20-diphenylporhinato]zinc(II)[1b] (**2**) that lacks donor and acceptor moieties. Notably, at 77 K, the linear absorption bands for **2** are considerably narrowed in comparison to **1** and exhibit less intense overtone components. In contrast to **1**, the electroabsorption spectrum for **2** (Panel C) is dominated by *first derivative* components (Panel B). In addition, the electroabsorption spectrum for **2** is 5- to 10-fold less intense than that observed for the D−A functionalized porphyrin for approximately the same sample concentration and applied external field. A fit of the spectrum in the Q-band region yields an extremely small absolute dipole moment change (0.5 ± 0.2 D) and a modest polarizability change ($\mathrm{Tr}(\Delta\alpha) = 60 \pm 20$ Å^3).[15] For the B_x and B_y bands, respectively, the molecular parameters are $\lvert\Delta\mu_{12}\rvert = 1 \pm 0.5$ and 0.35 ± 0.1 D

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(9) Interestingly, the angle, χ, between the transition dipole moment, P_{12}, and the change in dipole moment is ca. 5 ± 5° for the *x*-polarized (0,0) transitions, but 35 ± 5° for the corresponding (1,0) transitions. For transitions where the symmetry is defined exclusively by charge transfer interactions, collinearity would be expected. The apparently substantial deviation from 0° for the $Q_x(1,0)$ and $B_x(1,0)$ transitions might be indicative of vibronic coupling to higher states of differing symmetry, or simply to mixing of *x*- and *y*-polarized states. We note further that the hyper-Rayleigh technique will capture all vectoral components in subsequent hyperpolarizability measurements but that EFISH measurements will capture only “correctly aligned” components. An alternative explanation for the deviation in χ is that: (a) each transition contains additional unresolved (lower frequency) vibronic components and (b) each component features χ values that are close to zero, but the overlapping vibronic components exhibit widely varying $\Delta\mu$ values. Oh has shown via simple Stark spectral simulations that when these conditions are met, apparent χ values as large as 38° can be generated (Oh, Ph.D. Thesis, Department of Chemistry, Stanford University, 1991). In principle, this alternative explanation could be evaluated by obtaining higher resolution Stark and linear absorption spectra, presumably at liquid helium temperature where inhomogeneous broadening is less significant.

(10) Also accompanying the *x*-polarized transitions are comparatively large polarizability changes, as indicated by the magnitude of the B_x term. According to Liptay,[4] this term can be written as

$$B_x = {}^5\!/_2\mathrm{Tr}(\Delta\alpha) + 5\boldsymbol{R}^{(1)}\cdot\Delta\mu + (3\cos^2\chi - 1)[{}^3\!/_2\boldsymbol{m}\cdot\Delta\alpha\cdot\boldsymbol{m} - {}^1\!/_2\mathrm{Tr}(\Delta\alpha) + {}^3\!/_2\boldsymbol{R}^{(2)}\cdot\Delta\mu - \boldsymbol{R}^{(1)}\cdot\Delta\mu]$$

In the expression, $\mathbf{m}$ is the unit vector in the direction of the dipole moment and $\mathbf{R}^{(1)}$ and $\mathbf{R}^{(2)}$ are sums involving the products of the transition dipole moment and the transition polarizability tensor. At $\chi = 54.7°$, $B_x = {}^5\!/_2\,\mathrm{Tr}(\Delta\alpha) + 5\mathbf{R}^{(1)}\cdot\Delta\mu$. If the $\mathbf{R}^{(1)}$ term is neglected, then traces of the polarizability changes for the *x*-polarized transitions are ca. +600 Å^3. Alternatively, the magnitude of the $\mathbf{R}^{(1)}$ term can be estimated by invoking a two-state model (admittedly, perhaps not appropriate here). Following Shin et al. (*J. Phys. Chem.* **1996**, *100*, 8157), the $\mathbf{R}^{(1)}$ term scales as $(\Delta\mu)^2/E_{op}$. Correction of the experimental B_x values for $\mathbf{R}^{(1)}$ contributions then yields $\mathrm{Tr}(\Delta\alpha)$ values of ca. +450 Å^3, where the positive sign indicates that the excited state in each instance is more polarizable than the ground state. Large positive polarizability changes are generally indicative of significant excited-state interactions with multiple higher lying states.

and Tr($\Delta\alpha$) = 75 ± 8 and 31 ± 4 Å^3.[16] These findings clearly support the claim that it is the donor and acceptor entities that induce the observed large $\Delta\mu$ effects in the corresponding functionalized chromophore (**1**).

State-Specific Hyperpolarizability Contributions. The overall predicted hyperpolarizability is given by a sum of the two-level and three-level contributions:[17]

$$\beta = \sum_{n \neq g} \beta'_n + \sum_{n \neq g} \sum_{m \neq n} \beta'_{nm} \qquad (2)$$

where β'_n and β'_{nm} refer to the state-specific two-level and three-level contributions to the sum-over-states expression for β, g denotes the ground state, and n and m denote excited states.[18] The available $|\Delta\mu_{12}|$, transition dipole moment (P_{12}),[11] and E_{op} values[1,3] provide sufficient information for electronic and vibronic state specific contributions, $|\beta'|$, to the first-order hyperpolarizability of **1** to be calculated. In the two-level formulation these are given as:[19]

$$\beta'_n = \frac{6(P_{12})_n^{\,2}(\Delta\mu_{12})_n(E_{op})_n^{\,2}}{[(E_{op})_n^{\,2} - (2E_{inc})^2][(E_{op})_n^{\,2} - E_{inc}^{\,2}]} \qquad (3)$$

where E_{inc} is the energy of the incident light and E_{op} is the energy of the electronic transition of interest. Note that as the zero-frequency limit is approached, the energy denominators will increasingly favor contributions from lower energy excited states.[20]

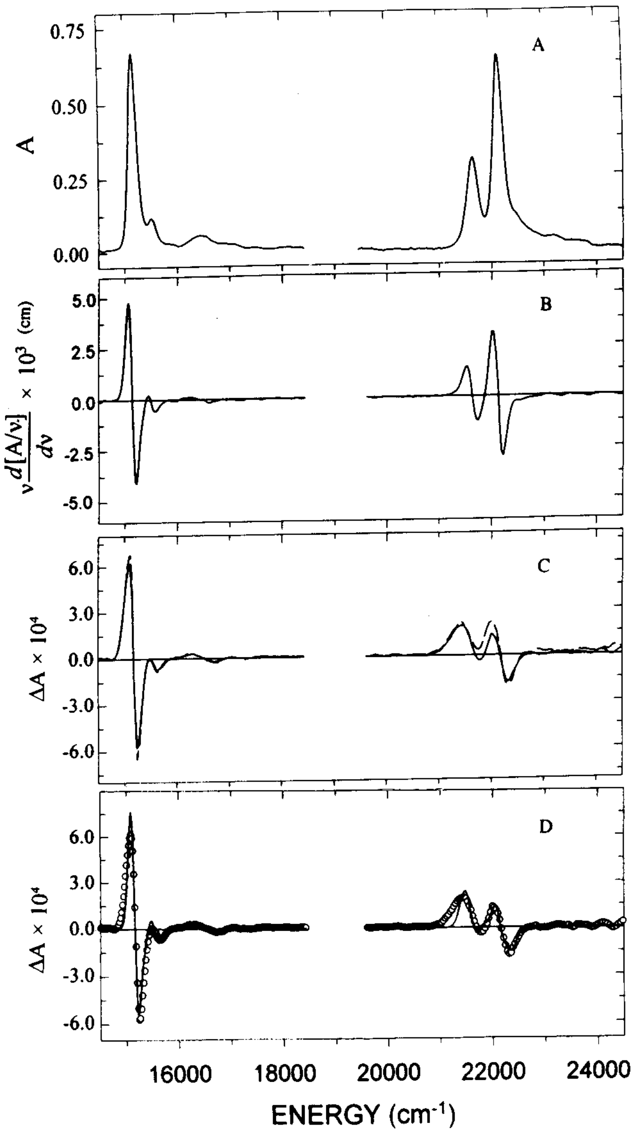

Figure 2. Panel A: Absorption spectrum of **2** in 2-mTHF glass at 77 K. Panel B: First derivative of the absorption band. Panel C: Electroabsorption response at $\chi = 90°$ (solid line) and 55° (dashed line). Panel D: Measured (circles) and fit (eq 1; solid line) electroabsorption spectra at 55°.

Table 1 summarizes the predicted two-level contributions to β from the seven lowest energy electronic transitions (B- and Q-bands) at various values of E_{inc}, including hypothetical conditions where E_{inc} is zero. The results largely corroborate

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(11) Transition dipole moments, P_{12}, were calculated by using the following expression:

$$P_{12} = (9.9 \times 10^{-2})(\epsilon_{max}\Delta\nu_{1/2}/E_{op})^{1/2}$$

Here ϵ_{max} is the extinction coefficient at the absorption maximum (M^{-1} cm^{-1}), $\Delta\nu_{1/2}$ is the bandwidth (cm^{-1}), and E_{op} is the absorption maximum (cm^{-1}) (Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A: Chem.* **1994**, *82*, 47).

(12) For the B_y transitions, the measured χ values are nearly 90°, implying orthogonality between the transition dipole moment and the change in dipole moment. Similar behavior has been reported by Liptay for *m*-nitroaniline species.[4]

(13) Electronic structure calculations coupled with FT, resonance, and transient resonance Raman spectroscopic studies support the notion that the excited state of compound **1** possesses charge-transfer character (ref 14). Consistent with these studies, our Stark spectroscopic data show that the magnitude of charge separation achieved with either B- or Q-band excitation is finite, but small. (Note that the separation of one unit charge over the 17.8 Å distance between the centroids of the two arylethynyl moieties would yield a dipole moment change of ~85 D.) The frontier orbitals for **1** have considerable porphyrin character, consistent with both strong coupling between the (4′-(dimenthylamino)phenyl)ethynyl and (4″-nitrophenyl)ethynyl moieties and the fact that electronically excited states of compounds in this structural class are highly delocalized.[1,3,14] To underscore this point, a simple Mulliken population analysis of ZINDO-derived frontier orbitals of **1** (standard INDO-1 semiempirical parameters, CI level = 20) shows that relative to the HOMO, the charge residing on the (4″-nitrophenyl)ethynyl group in the LUMO is augmented by 0.16 electrons while the (4′-(dimethylamino)phenyl)ethynyl and porphyrin units are depleted in charge by 0.09 and 0.07 electrons, respectively.[14] A similar redistribution of electronic charge occurring within the B_x and Q_x states of **1** would give rise to values of $\Delta\mu_{12}$ of comparable magnitude to those listed in Table 1.

(14) LeCours, S. M.; Philips, C. M.; de Paula, J. C.; Therien, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 12578−12589.

(15) The Q and B bands were each fit to eq 1 by using three parameters (i.e. the overall band in each region was treated as a single electronic transition). Due to the narrowness of the B band linear absorption and the relatively large spectral band-pass employed in the electroabsorption experiment, signals for the latter may be artificially broadened. In any case, the apparent changes in polarizability upon excitation of **2** are qualitatively similar to those reported by Davidsson (*Chem. Phys.* **1980**, *45*, 409−414) for free base tetraphenylporphyrin.

(16) For compound **2**, only the Tr($\Delta\alpha$) component of B_x is likely to contribute to the first derivative signal since the associated changes in dipole moment are vanishingly small (see ref 10).

(17) (a) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195. (b) Kanis, D. R.; Lacroix, G. P.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10089. (c) Kanis, D. R.; Marks, T. J.; Ratner, M. A. *Nonlinear Opt.* **1994**, *6*, 317.

(18) Recall that the term "two-level" refers to each contribution to the sum-over-states expression (i.e., the ground level and one other level). The summation is then carried out over all available states (in this case seven observed excited states).

(19) (a) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664. (b) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446. (c) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590.

(20) It should be noted that eqs 2 and 3 were derived for multiple electronic excited states. In the absence of appropriate theory, we have used eqs 2 and 3 to account also for multiple vibronic excited state contributions. We recognize that for hyper-Rayleigh scattering under resonant conditions, the approach almost certainly is not fully correct. (For example, it would predict significant destructive vibronic interference effects that have *not* been observed in excitation profile studies.) We suggest that under pre- and/or post-resonant conditions, however, eq 3 should prove semiquantitatively applicable to studies entailing sums over vibronic states.

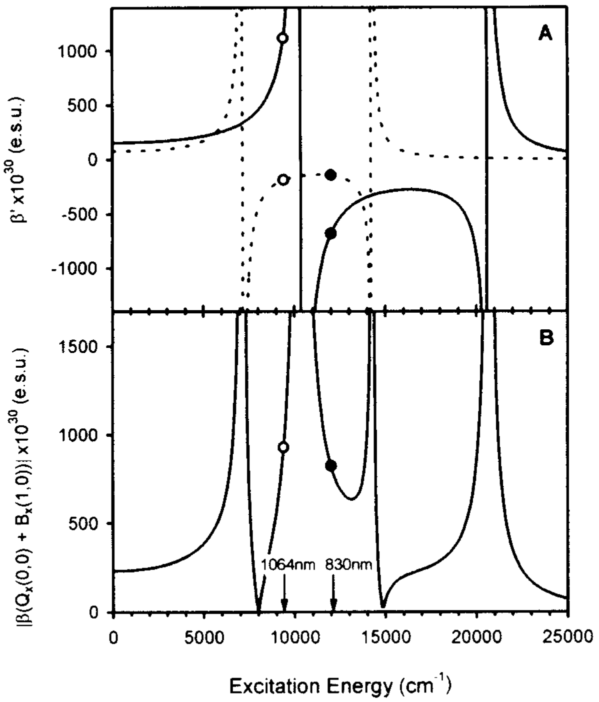

Figure 3. Panel A: Calculated two-level (eq 2) incident energy dependence of β' for $Q_x(0,0)$ (dashed line) and $B_x(1,0)$ (solid line) transitions based on vibrationally resolved (low temperature) oscillator strengths, transition energies, and $\Delta\mu_{12}$ values, where all $\Delta\mu_{12}$ values are assumed to be positive. Panel B: Calculated combined two-level response for $Q_x(0,0)$ and $B_x(1,0)$. For simplicity, contributions to β from other electronic and vibronic transitions have been omitted.

the findings obtained from an analysis of the NLO properties of compound **1** that utilized the sum-over-states approach for electronic states calculated by semiempirical methods (INDO/SCI).[3] Most notably, they verify—essentially quantitatively—the significance of *x*-polarized B transitions, while confirming the marginal role of the analogous *y*-polarized transitions. The electroabsorption experiments, however, also reveal important contributions from Q-band transitions not predicted by theory. The addition of the newly identified Q-band dipole moment contributions to the previously calculated sum-over-states estimate of β increases the predicted zero-frequency nonlinear response (β_0)[21] by about 20%, but the reason for the predicted lack of importance for the Q_x transitions in the calculation remains unclear.[3] (We assume, following Scheme 1 and the work of Priyadarshy et al.,[3] that all two-level contributions to β_0 (Table 1) are positive. Note, however, that because isotropic electroabsorption measurements yield only absolute values for $\Delta\mu_{12}$, the sign of β' must be determined or inferred independently.)

Excitation Frequency Effects. Perhaps more important than the zero-frequency contributions are the predicted Q- and, especially, B-band contributions at finite frequency. As shown in Figure 3, $\beta'(Q_x)$ initially increases as the incident light energy is increased in the near-infrared region. Similar effects are calculated for the B transitions, which contribute much more significantly to β when 4000 cm^{-1} < $E_{\mathrm{inc}} \leq$ 9398 cm^{-1}. From eqs 2 and 3 (two-level terms only)[22] and the available electroabsorption data, the predicted nonlinear responses (based on combined Q- and B-band contributions; cf. Figure 3) are 340 × 10^{-30}, 540 × 10^{-30}, 1710 × 10^{-30}, and −1220 × 10^{-30} esu at E_{inc} = 0, 5244 (1907 nm), 9398 (1064 nm), and 12 048 cm^{-1} (830 nm), respectively. (If *y*-polarized contributions are neglected, the calculated β values are 290 × 10^{-30}, 480 × 10^{-30}, 1490 × 10^{-30}, and −920 × 10^{-30} esu at 0, 5244, 9398, and 12 048 cm^{-1}, respectively.) Notably, from the analysis in Figure 3 (see also Table 1) the apparent experimental frequency independence of β is evidently due to similar *absolute* hyper-Rayleigh scattering efficiencies at 830 and 1064 nm. The analysis predicts that (a) the sign of β will be reversed at 1064 nm in comparison to 830 nm (a prediction that, in principle, could be tested via EFISH measurements) and (b) the magnitude of β will change drastically at intermediate excitation wavelengths.

Table 1 together with eq 2 provides some additional insight into the likely origin of the large second-order responses from **1**. From the table, the single largest contributor to $\beta(1064)$ is evidently the $B_x(1,0)$ transition. This transition is both strongly allowed and nearly two-photon resonant (i.e. $E_{\mathrm{op}} \approx 2E_{\mathrm{inc}}$). Furthermore, because the corresponding absorption band is comparatively sharp, resonance damping effects (neglected in eq 2) are expected to be relatively unimportant. Note also that $\beta'(B)$ and $\beta'(Q)$ have opposite signs and therefore partially cancel.

If the excitation wavelength of incident light is shifted to 830 nm, the two-photon resonance term in eq 2 ($[E_{\mathrm{op}}^2 - (2E_{\mathrm{inc}})^2]^{-1}$) becomes less significant for the $B_x(1,0)$ transition, making it comparatively less important. In contrast to the behavior at 1064 nm, however, the $\beta'(B)$ and $\beta'(Q)$ contributions now have identical signs. The calculated total first hyperpolarizability, therefore, is only slightly smaller at 830 nm than at 1064 nm. (Note that the two-photon resonance achieved with the B_y transitions of **1** based on 830 nm excitation is anticipated to be of little consequence since these transitions are largely Stark silent.)

Finally, the two-photon resonance phenomenon appears to account for the qualitatively different incident-light wavelength dependence of hyper-Rayleigh scattering from the (porhinato)-copper(II) analogue (**3**) of compound **1**. The distinguishing chromophoric features of **3** in comparison to **1** are (a) a ~700 cm^{-1} blue shift in the B-band transitions and (b) a ~450 cm^{-1} blue shift in the Q-band transitions. The results of calculations[23] like those in Table 1, but for chromophore **3**, show that the seemingly modest energy shifts significantly diminish the otherwise substantial scattering contributions from the $B_x(1,0)$ and the $B_x(0,0)$ transitions when the wavelength of the incident light is 1064 nm. The calculated decrease is pronounced because the spectral shifts significantly affect the two-photon resonance term in the denominator of eq 2. When the wavelength of incident light is shifted to 830 nm, the key transitions (i.e. $B_x(1,0)$ and $B_x(0,0)$) are more strongly two-photon resonant than at 1064 nm. Consequently, the small overall energy shifts entailed in replacement of zinc by copper in the chromophoric assembly yield substantial relative changes in the energy denominator in eq 2, inducing considerable changes in β' values. In any case, when contributions from all seven visible-region transitions are considered, β_{830} for the copper-containing chromophore is −1470 × 10^{-30} esu and β_{1064} is 960 × 10^{-30} esu. Thus, the calculated incident-light wavelength dependence of β for **3** is in reasonable qualitative

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[21] The ZINDO based sum-over-states calculation (*three* level) yielded a β_0 value of ~175 × 10^{-30} esu (see ref 2).

[22] The predicted contributions from three-level interactions (ground state, Q-band, and B-band excited states) are positive for 0, 5244 (1906 nm), and 12 048 cm^{-1} (830 nm) excitation, but negative for 9398 cm^{-1} (1064 nm) excitation. Unfortunately, we lack the necessary experimental excited-state to excited-state transition dipole moment information to make quantitative predictions.

[23] We have assumed, for simplicity, that dipole moment changes and oscillator strengths for **3** are the same as those measured for **1**.

agreement with the decrease in absolute hyper-Rayleigh scattering efficiency found experimentally for **3** upon shifting from 830 nm excitation to 1064 nm excitation.

Conclusion

Electroabsorption studies show that the push−pull chromophore, **1**, displays large changes in dipole moment for both the Q and B (Soret) transitions. The dipole moment effects evidently arise from charge-transfer perturbations induced by appended arylethynyl donor and acceptor functionalities. These effects in turn conspire to produce unusually large absolute enhancements of β in the near-infrared region, and coincidentally identical $|\beta|$ values for 830 nm versus 1064 nm excitation. The dominant contributor to the molecular first hyperpolarizability in all spectral regions derives largely from x-polarized transitions in the Soret region, though at long wavelength, the Q_x transition plays a significant role in determining the overall magnitude of β. For the corresponding copper-containing chromophore, **3**, slight shifts in B-band energies significantly diminish the two-photon enhancement effect when $E_{\mathrm{inc}}^{-1} = 1064$ nm, but slightly increase the enhancement effect when $E_{\mathrm{inc}}^{-1} = 830$ nm. Consequently, the absolute hyper-Rayleigh scattering efficiency for **3** displays a much more pronounced dependence on excitation wavelength than the scattering efficiency for **1**, at least when comparisons are limited to 830 and 1064 nm irradiation. Finally, for **1**, inclusion of contributions from Q_x transitions yields a zero-frequency nonlinear optical response (sum-over-states two-level calculation) that is in reasonably good agreement with the value inferred from low-frequency EFISH measurements.

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Supporting Information Available: A figure showing the field dependence of the electroabsorption spectrum in the B band region (1 page; print/PDF). See any current masthead page for ordering information and Web access instructions.

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