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# Push−Pull Arylethynyl Porphyrins: New Chromophores That Exhibit Large Molecular First-Order Hyperpolarizabilities

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**Abstract:** A new class of chromophores has been fabricated that features both electron-releasing and electron-withdrawing groups fused via an intervening ethynyl moiety to the carbon framework of a (porphinato)metal complex. These species possess large molecular first-order hyperpolarizabilities ($\beta$). We report herein the synthesis, optical spectroscopy, and the hyper-Rayleigh scattering data used to determine the $\beta$ values of two archetypal members of this new class of exceptional nonlinear chromophores: [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)-ethynyl]-10,20-diphenylporphinato]copper(II) and [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphinato]zinc(II). One of these compounds, [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphinato]zinc(II), possesses $\beta$ values near $5000 \times 10^{-30}$ esu at incident irradiation wavelengths of both 830 and 1064 nm. These studies suggest that this chromophoric structural motif may find utility in the development of electrooptic devices as well as materials for efficient frequency doubling of incident irradiation (second harmonic generation).

## Introduction

Future generations of optoelectronic devices for telecommunications, information storage, optical switching, and signal processing are predicated to a large degree on the development of materials with exceptional nonlinear optical (NLO) responses.[1] Toward this end, considerable effort has been spent to elucidate the chromophore design elements that correlate most closely with large first-order hyperpolarizabilities; this is due to the fact that an NLO chromophore with an exceptional molecular first hyperpolarizability would be a highly desirable candidate for incorporation into electric field poled-polymeric systems and thus serve as the basis for macroscopic materials for frequency doubling as well as electrooptical devices that function as waveguide switches, modulators, filters, and polarization transformers.[1d]

A tremendous number of chromophores has been evaluated for suitability to function as components in hypothetical NLO materials. A few of these chromophores have served as components of functioning polymer-based optoelectronic devices; the physical properties of all these prototype materials possess one or more critical deficiencies that render commercialization of these systems impractical.[1−10] These facts suggest that it may be appropriate to reexamine the accepted tenets of NLO chromophore design and that new types of chemical systems should be examined in this regard if significant advances are to be realized. Toward such ends, our group has focused on new approaches to regulate chromophore photophysical properties.[11−16] We report herein a new set of engineering criteria for large molecular first-order NLO responses; these design notions are manifest in a porphyrin-based NLO chromophore structural motif that not only provides for significant molecular first hyperpolarizabilities, but also displays exceptional thermal stability as well.

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## Experimental Section

**Materials.** All compounds were handled using methods and protocols described previously.[15] Elemental analyses were performed at Robertson Microlit Laboratories (Madison, NJ).

**Instrumentation**. Electronic spectra were recorded on an OLIS UV/vis/NIR spectrophotometry system that is based on the optics of a Carey 14 spectrophotometer.

**Hyper-Rayleigh Light Scattering (HRS) Experiments.** The details of the method[17,18] as well as the experimental set up at the University of Nebraska have been presented previously.[18] Normally, the first-order nonlinear effect is absent in an isotropic medium because of the centrosymmetric environment; removal of centrosymmetry and measurement of the molecular first hyperpolarizability has most commonly been accomplished by the electric field-induced second harmonic generation (EFISH) technique. The primary advantage of the HRS method lies in the fact that no external electric field is necessary for the experiment, since thermal motion constantly distorts the local symmetry of the medium, removing instantaneously centrosymmetry in the liquid and allowing incoherent second harmonic light to be observed. It is important to note that the HRS technique is very sensitive to solution concentration; it is thus an ideal method for the evaluation of the hyperpolarizabilities of the high extinction coefficient porphyrin-derived chromophores reported in this paper.

Nd:YAG (10 Hz; 3−8 ns pulse width) and Ti-sapphire lasers (Coherent, Mira Model 9000; 76 MHz; 100 fs pulse width) were used as excitation sources. The intensity of the incident beam from the Nd:YAG laser, after it was filtered through a set of three long pass filters to remove the second harmonic component at 0.53 $\mu$m, was varied via the combination of a polarizer with a multiple-order half wave plate. The incident beam was focused onto the sample with a f/10 lens and the scattered light was collected by a f/1.3 lens followed by a biconvex lens with a focal length of 30 cm. The collected signal was directed to a photomultiplier tube equipped with an interference filter and a sharp bandpass filter set at the second harmonic frequency attached in the front. A boxcar integrator was used to process the signal when the Nd:YAG laser was used as an excitation source. To take advantage of its high repetition rate, a photon counting system was utilized to process the light scattering signal when the Ti-sapphire laser was used as an excitation source. All HRS experiments were carried out at room temperature. The scattering angle was 90°.

Samples for HRS studies were dissolved in chloroform ($CHCl_3$) and filtered through a 0.2 $\mu$m membrane to remove dust and any adventitious particulates. Samples differing in chromophore concentration were prepared by serial dilution of a concentrated standard. Glass solution cells (3.5 mL) were used throughout these experiments.

**(5,15-Dibromo-10,20-diphenylporphinato)zinc(II) and 4-Substituted Phenylacetylenes.** [*p*-(Dimethylamino)phenyl]acetylene and (*p*-nitrophenyl)acetylene were synthesized similarly to literature methods.[19] The preparation of (5,15-dibromo-10,20-diphenylporphinato)zinc(II) has been previously reported.[15]

**[5-[[4′-(Dimethylamino)phenyl]ethynyl]-15-bromo-10,20-diphenylporphinato]zinc(II).** (5,15-Dibromo-10,20-diphenylporphinato)zinc(II) (252 mg, 369 $\mu$mol), CuI (10 mg, 52 $\mu$mol), Pd[$PPh_3$]$_4$ (35 mg, 30 $\mu$mol), diethylamine (5 mL), and [*p*-(dimethylamino)phenyl]acetylene (63.1 mg, 435 $\mu$mol) were brought together along with 30 mL of tetrahydrofuran (THF) in a 100 mL Schlenk tube under an $N_2$ atmosphere. The resulting solution becomes intensely green as the reaction proceeds at room temperature. At the reaction endpoint ($t$ = 12 h), the crude product was purified by column chromatography on silica gel using 4:1 hexanes:THF as eluant. The green band was collected and evaporated to give a deep green (almost black) residue (97.5 mg, 35%).

**[5-[[4′-(Dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphinato]zinc(II) [1(Zn$^{II}$)].** [5-[[4′-(Dimethylamino)phenyl]ethynyl]-15-bromo-10,20-diphenylporphinato]zinc(II) (52.0 mg, 102 $\mu$mol), (*p*-nitrophenyl)acetylene (35.2 mg, 240 $\mu$mol), Pd[$PPh_3$]$_4$ (15.0 mg, 13 $\mu$mol), and copper(I) iodide (6.6 mg, 35 $\mu$mol) were placed in a 50 mL Schlenk tube under an $N_2$ atmosphere. THF (10 mL) and diethylamine (1 mL) were added. The reaction vessel was shielded from light and allowed to react at room temperature. After 12 h, the solution was evaporated to dryness and the solid purified by column chromatography (silica gel, 3:1 hexanes:THF). The green band was collected and dried to give the desired product (57.0 mg, 97%). $^1$H NMR (250 MHz, $CDCl_3$, pyridine-$d_5$): $\delta$ 9.63 (d, 2 H, $J = 4.6$), 9.51 (d, 2 H, $J = 4.6$), 8.78 (d, 2 H, $J = 4.6$), 8.73 (d, 2 H, $J = 4.6$), 8.10 (m, 6 H), 7.83 (d, 2 H, $J = 8.7$), 7.75 (d, 2 H, $J = 8.9$), 7.64 (m, 6 H), 6.69 (d, 2 H, $J = 8.8$), 2.93 (s, 6 H). $^{13}$C NMR (60 MHz, $CDCl_3$, pyridine-$d_5$): $\delta$ 152.06, 151.46, 150.08, 149.93, 146.13, 142.40, 134.25, 132.66, 132.55, 131.94, 131.31, 131.11, 130.79, 129.84, 127.23, 126.29, 123.60, 122.73, 111.82, 110.49, 104.14, 99.67, 98.58, 97.52, 94.11, 91.23. Vis (THF): 460 (5.27), 678 (4.88). FAB MS: 812.19 (calcd 812.19). Anal. Calcd for $C_{54}H_{40}N_6O_3Zn\cdot C_4H_8O$(THF): C, 73.18; H, 4.55; N, 9.48. Found: C, 73.04; H, 4.48; N, 9.40.

**[5-[[4′-(Dimethylamino)phenyl]ethynyl]-15-[(4″-(nitrophenyl)-ethynyl]-10,20-diphenylporphinato]copper(II) [1(Cu$^{II}$)].** A 20.6 mg (25.3 $\mu$mol) amount of analytically pure **1(Zn$^{II}$)** was dissolved in 50 mL of a 1:1 THF:$CHCl_3$ solution in a 125 mL Erlenmeyer flask. Concentrated hydrochloric acid (0.5 mL) was added dropwise. After 5 min, triethylamine (5 mL) was added. The mixture was stirred an additional 5 min before being placed into a 125 mL separatory funnel. The organic layer was washed once with 1.0 M KOH (20 mL) and then with distilled water. The aqueous fractions were discarded, and the organic layer was rotovapped to dryness. The free base push−pull (arylethynyl)porphyrin was used without further purification. Vis (THF): 446, 624, 708.

The 5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[4″-(nitrophenyl)ethynyl]-10,20-diphenylporphyrin was placed in a 200 mL round bottom flask equipped with a stir bar. Toluene (60 mL) and cupric acetate hydrate (100 mg, 501 mmol) were added. The resulting mixture was heated to reflux. After 6 h, the mixture was cooled and placed in a 125 mL separatory funnel. The toluene layer was washed once with a 1 M ammonium hydroxide solution (50 mL) and then twice with water (50 mL). The toluene layer was rotovapped to a total volume of approximately 15 mL and then chromatographed on silica gel using toluene as eluant. A tight, single green band was rotovapped to dryness and further dried under high vacuum to give **1(Cu$^{II}$)** [12.0 mg, 58% based on 20.6 mg of compound **1(Zn$^{II}$)**]. Vis (THF): 452 (5.19), 656 (4.74). Low resolution FAB MS: 812 (calcd 811).

## Results and Discussion

Design, modification, and further fine-tuning of the magnitude of the molecular first hyperpolarizability ($\beta$) of a given chromophore has generally been thought of in the context of Oudar's two-state model:[2−4]

$$\beta \propto (\mu_{ee} - \mu_{gg})\frac{\mu_{ge}^2}{E_{ge}^2} \qquad (1)$$

Here $g$ and $e$ represent the indices of the ground and charge transfer (CT) excited states, respectively; $\mu$ is the dipole matrix element and $E$ is the transition energy. The dominant component of the $\beta$ tensor is thus seen to be proportional to the change in dipole moment between the ground and excited states as well as the square of the transition oscillator strength, while inversely proportional to the square of the energy gap between these two states.

Most NLO chromophores are composed of a donor (D) and acceptor (A), which are the molecular entities chiefly involved

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in charge redistribution, as well as a bridge, which we define as the molecular scaffolding that links the D and A portions of the molecule. To date, the design of chromophores with good second-order nonlinear properties has focused primarily on engineering: (i) the electronic nature of the D and A, and (ii) the conjugation length of the bridge.[5−10] The former controls D−A mixing with respect to a specific bridge, while the latter plays a role in modulating D−A electronic coupling as well as determines the magnitude of the change in dipole moment. It is important to recognize that the parameters $\mu_{ee} - \mu_{gg}$, $\mu^2{}_{ge}$, and $E^2{}_{ge}$ are all intimately related: for example, increasing the bridge conjugation length, in general, results in an increase in the magnitude of the ground-to-excited state change in dipole moment, while concomitantly diminishing the square of the dipole matrix element and augmenting the square of the CT transition energy; the latter two effects have their genesis in the fact that increased bridge lengths abate D−A electronic coupling. Maximizing $\beta$ thus involves a subtle interplay between three parameters that do not necessarily simultaneously attain their optimal value for a particular molecular structure (D, A, bridge); thus, optimization of the first hyperpolarizability, $\beta$, obviously involves a balancing act.[20]

The overwhelming number of chromophores that have been studied to date for their second-order nonlinear properties can be classified as D−A systems in which the molecular bridge is either based on ethene, phenylene, ethyne, small-ring heteroaromatic, or styrene building blocks, or a combination of two or more of these simple units. Although a variety of different organic media have been utilized as D−A bridging moieties, comparatively little attention has been paid to how the details of the bridge topology and electronic structure impact the chromophore second-order NLO response, particularly when viewed alongside the tremendous body of literature describing how D−A electronic properties and bridge length modulate the molecular first hyperpolarizability.[5−10]

The bridge mediated donor−acceptor electronic interaction must be large in order to maximize the strength of the transition matrix element (associated with the oscillator strength) of the charge-transfer transition. Yet, if this D−A bridge-mediated mixing is too large, the D and A states will be strongly mixed together and the molecule will lose its electronic asymmetry (that is, the dipole moment difference between the ground and excited states). In the extreme limit where all asymmetry is lost, there is no dipole moment change between ground and excited state, so $\beta$ is diminished within the context of the two-state model.[2−4]

Some simple models for NLO chromophores that capture the essence of the problem are cast in a four-orbital framework: two of these orbitals correspond to the donor- and acceptor-localized states and two to the bridge frontier orbitals.[20] Within this four-orbital description, a control parameter Δ can be defined that is approximately related to the relative orbital energies of the isolated donor (HOMO) and isolated acceptor (LUMO) orbitals ($E_D$ and $E_A$, respectively) in units of the effective coupling interaction ($t'$) between D and A provided by the bridge.

$$\Delta = (E_D - E_A)/|t'| \qquad (2)$$

The magnitudes of $\mu_{ee} - \mu_{gg}$, $\mu^2{}_{ge}$, and $E^2{}_{ge}$ will be effected by the dimension of the parameter Δ;[20] that Δ depends intimately on the nature of the bridge highlights the need to explore new types of molecular scaffolding to connect D to A in NLO chromophores.

In an effort to construct entirely new classes of NLO chromophores with exceptional photophysical properties, we have focused on engineering bridge electronics and topology. Our most basic criterion is that the bridge should be much more polarizable than the simple polyene, polyyne, polyphenylene, and polyheteroaromatic structures that have been most commonly used. Moreover, the bridge must be the primary photonic component of the molecule in the sense that a significant portion of the oscillator strength of the charge transfer transition that couples D to A should be bridge localized. Ideally, the bridge-localized excited state should dramatically alter D−A electronic coupling relative to the coupling the ground-state bridge provides.

One approach to enabling such differential ground- and excited-state coupling is to choose a D−A bridging motif that is capable of accessing a resonance form in its excited state that is unattainable for the ground-state structure. Such an excited-state resonance structure would be optimal if it produced a large transition dipole oriented directly along the D-to-A molecular charge transfer axis. A designed excited state with these properties would facilitate large molecular first hyperpolarizabilities since the magnitude of the change in dipole moment would not be held ransom by significant diminution of the oscillator strength of the CT transition or an increase in the transition energy at relatively large D−A distances, since a high oscillator strength, bridge-centered transition would now directly couple D to A. Presumably in such a system, if the orientation and dipolar nature of the bridge-centered CT transition could be maintained over a long range, $\mu_{ee} - \mu_{gg}$ and $\mu^2{}_{ge}$ would simultaneously increase with augmented bridge lengths while concomitantly maintaining or slightly reducing $E^2{}_{ge}$.

Many of these desirable design elements for the bridge in such an NLO chromophore have already been realized. We have reported the synthesis and optical spectroscopy of a variety of ethynyl- and butadiynyl-linked porphyrin arrays.[11] A subset of this new class of compounds is one in which ethynyl groups are utilized to attach multiple porphyrins together at their respective *meso*-carbon positions; the excited states of some of these species, exemplified by [5,15-bis[[5′-[(10,20-diphenylporphinato)zinc(II)]]ethynyl]-10,20-diphenylporphinato]zinc(II), possess substantial dipole moments.[11,12] Such large transition dipoles derive in part from the extended conjugation enabled by the approximate coplanarity of the porphyrin macrocycles in solution. Fast time-resolved anisotropy measurements show that the excited state of such multichromophoric systems is singly degenerate and oriented along the $C_2$ molecular axis of highest conjugation.[12b]

Porphyrin conjugation can be extended when the ethynyl group is used to link the chromophore to an aromatic entity other than porphyrin. We have synthesized a variety of symmetrically-substituted [5,15-bis(arylethynyl)-10,20-diphenylporphinato]metal complexes;[13] like the *meso*-to-*meso* ethynyl-bridged porphyrin arrays, the electronically excited states of these species show substantial energetic splitting between *x*- and *y*-polarized populations, with the short-time anisotropy consistent with a singly degenerate excited state localized along the molecular axis defined by the arylethynyl groups.[14]

Using a modification of the synthetic procedures developed to assemble the conjugated porphyrin arrays and the 5,15-bis(arylethynyl)-10,20-diphenylporphyrins,[13,15] one can fabricate asymmetric, arylethynyl-elaborated porphyrins. Scheme 1 shows the synthesis of [5-[[4′-(dimethylamino)phenyl]ethynyl]-

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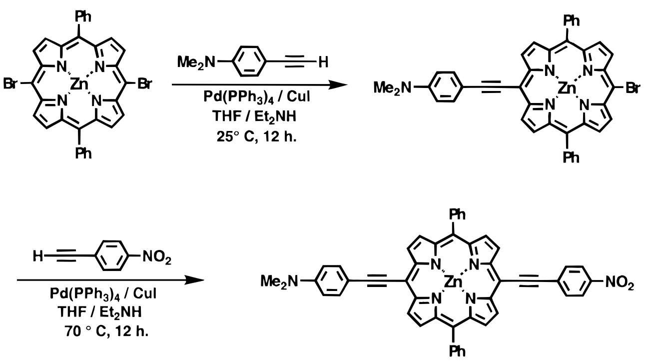
**Scheme 1**



15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphinato]zinc(II) [**1(Zn$^{II}$)**], the archetypal member of a new class of D–A chromophores, the push–pull (arylethynyl)porphyrins.

Photophysical studies of **1(Zn$^{II}$)** and its (porphinato)copper analogue, **1Cu$^{II}$,** show that these species possess a host of unusual optical properties.[14,16] For example, transient resonance Raman studies indicate that the excited states of [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[4″-(nitrophenyl)ethynyl]-10,20-diphenylporphinato]metal complexes exhibit reduced bond order in the 4′-(dimethylamino)phenyl and 4″-nitrophenyl aryl rings as well as in the nitro group with respect to that seen for these modes in their ground-state spectra; downshifting of these vibrational frequencies is not observed when the transient excited-state resonance Raman spectrum is compared with the analogous ground-state spectrum for the corresponding symmetrically-substituted (arylethynyl)porphyrins such as [5,15-bis-[[4′-(dimethylamino)phenyl]ethynyl]-10,20-diphenylporphinato]-metal complexes.[16] Scheme 2 summarizes this data and presents our current picture of the excited state of **1(Zn$^{II}$)**, **1(Zn$^{II}$)***; note that **1(Zn$^{II}$)*** can access a cumulenic resonance form while **1(Zn$^{II}$)** is best described as a supramolecular chromophore in which three aromatic ring systems are linked by ordinary carbon–carbon single and triple bonds.

Since the push–pull (arylethynyl)porphyrin structural motif in fact displays two of the proposed elements we thought key to the fabrication of exceptional NLO chromophores, namely a highly-polarizable D–A bridge that (i) contains significant oscillator strength and (ii) provides spectacular D–A electronic coupling in its excited state with respect to its ground state, we examined the molecular first hyperpolarizabilities of two [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphinato]metal complexes, **1(Zn$^{II}$)** and [5-[[4′-(dimethylamino)phenyl]ethynyl]-15-[(4″-nitrophenyl)ethynyl]-10,20-diphenylporphinato]copper(II) [**1(Cu$^{II}$)**], using the hyper-Rayleigh (light) scattering (HRS) technique.[17,18]

Measurements of the molecular first hyperpolarizability for both **1(Zn$^{II}$)** and **1(Cu$^{II}$)** were carried out in chloroform solvent for incident irradiation wavelengths of 830 ($\lambda_1$) and 1064 ($\lambda_2$) nm. Figure 1 shows the electronic absorption spectra of **1(Zn$^{II}$)** and **1(Cu$^{II}$)**. Note that the scattered light at the second harmonic of 830 nm (0.5 $\lambda_1$) will be partially absorbed by both chromophores on the blue shoulder of the Soret transition, while scattered light of wavelength 532 nm (0.5 $\lambda_2$) corresponds to a frequency in the optically-transparent region of the spectra of both **1(Zn$^{II}$)** and **1(Cu$^{II}$)**. HRS data obtained at incident irradiation wavelength $\lambda_1$ were Beer's Law-corrected for chromophore absorption to eliminate the effective signal attenuation prior to calculating $\beta_{830}$ using an approach described previously.[18]

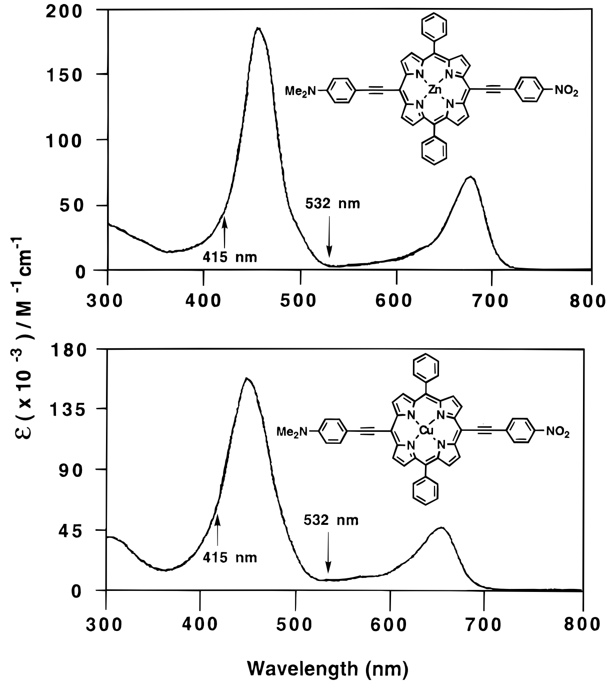


**Figure 1.** Electronic spectra of **1(Cu$^{II}$)** and **1(Zn$^{II}$)** recorded in chloroform. Arrows at 532 and 415 nm indicate the wavelengths corresponding to the second harmonic of the fundamental incident 1064 and 830 nm irradiation, respectively.

The total scattered light intensity at 0.5 $\lambda$ ($2\omega$) is given by:

$$\boldsymbol{I}(2\omega) = \boldsymbol{K}(\rho_s\beta_s^2 + \rho_c\beta_c^2)\boldsymbol{I}(\omega)^2 \qquad (3)$$

where $\rho_S$ and $\rho_C$ are the number densities of solvent and chromophore molecules, $\beta_S$ and $\beta_C$ the major hyperpolarizability tensor of the solvent and chromophore, $\omega$ the frequency of incident irradiation, $2\omega$ the second harmonic frequency, $I$ the light intensity, and $K$ a quantity determined only by the scattering geometry and local field factors at low chromophore concentrations. Figures 2 and 3 plot the hyper-Rayleigh scattering signal at $I(2\omega)$ versus chromophore number density for **1(Zn$^{II}$)** and **1(Cu$^{II}$)** in chloroform solvent in the very dilute concentration regime for irradiation at wavelengths $\lambda_1$ and $\lambda_2$; $\beta_{830}$ and $\beta_{1064}$ for both chromophores can be directly evaluated from these plots.[18] Non-negative intercepts were obtained in all cases at low chromophore concentrations. The quadratic dependence of $I(2\omega)$ on I($\omega$) verified that the scattered light intensity clearly arises from the nonlinear hyper-Rayleigh scattering process (data not shown). The evaluated chromophore molecular first hyperpolarizabilities were referenced internally against the known solvent $\beta$ value; the well-studied NLO chromophore *p*-nitroaniline (PNA) was used as an external reference in these experiments.[21] Consistent $\beta$ values were obtained irrespective of the choice of reference.

The $\beta$ values evaluated from the data presented in Figures 2 and 3 are exceptionally large. The wavelength dependence of the molecular first hyperpolarizability for **1(Cu$^{II}$)** shows that changing the incident irradiation wavelength from 830 to 1064 nm results in a decrease in the magnitude of the evaluated $\beta$ by approximately 65% ($\beta_{830} = 4374 \times 10^{-30}$ esu; $\beta_{1064} = 1501 \times 10^{-30}$ esu). The data obtained for **1(Zn$^{II}$)** in chloroform is exceptionally intriguing: in contrast to that seen for **1(Cu$^{II}$)**, the measured $\beta$ value appears to be virtually indepen-

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[21] Internal reference, CHCl$_3$ solvent: $\beta_{\text{(chloroform)}} = -0.49 \times 10^{-30}$ esu. External reference, *p*-nitroaniline (PNA) in CHCl$_3$: $\beta_{\text{(PNA)}} = 23 \times 10^{-30}$ esu at 1.06 $\mu$m (HRS); $\beta_{\text{(PNA)}} = 25 \times 10^{-30}$ esu at 1.06 $\mu$m (EFISH).

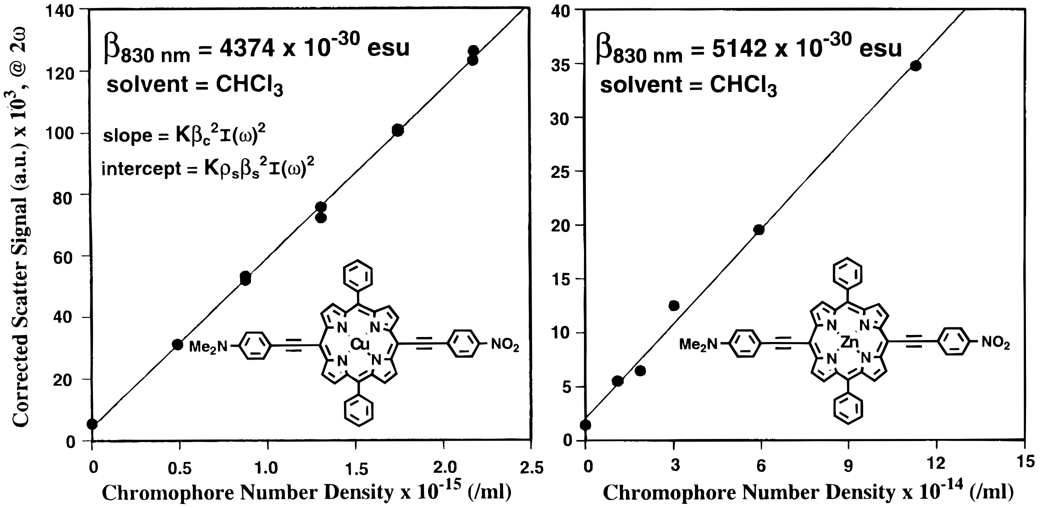


**Figure 2.** Hyper-Rayleigh scattering signal (corrected for absorption) vs chromophore number density for **1(Cu$^{II}$)** and **1(Zn$^{II}$)** in chloroform; excitation source = Nd:YAG laser. The solid line represents the best fit to the data points as described in the text. The quantities ($\rho_s$, $\beta_s$) and ($\rho_c$, $\beta_c$) denote the concentration and hyperpolarizabilty of solvent molecules and chromophores, respectively.

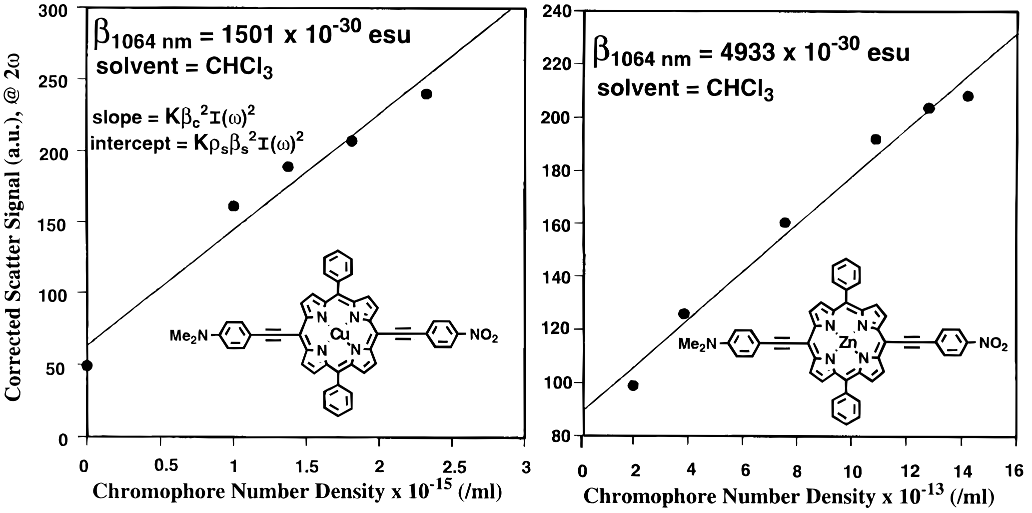
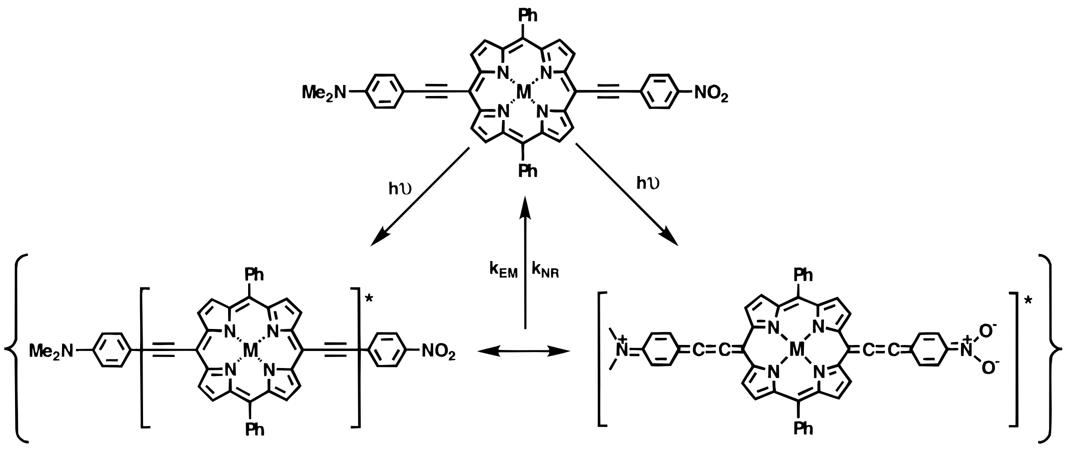


**Figure 3.** Hyper-Rayleigh scattering signal (corrected for absorption) vs chromophore number density for **1(Cu$^{II}$)** and **1(Zn$^{II}$)** in chloroform; excitation source = Ti-Sapphire laser. The solid line represents the best fit to the data points as described in the text. The quantities ($\rho_s$, $\beta_s$) and ($\rho_c$, $\beta_c$) denote the concentration and hyperpolarizabilty of solvent molecules and chromophores, respectively.

**Scheme 2**



dent of irradiation wavelength ($\beta_{830}$ = 5142 × $10^{-30}$ esu; $\beta_{1064}$ = 4933 × $10^{-30}$ esu).

While theoretical studies based on INDO/SCI calculations within a sum over states formalism are consistent with the very large, experimentally determined molecular first hyperpolarizabilities of the push–pull (arylethynyl)porphyrin complexes,[22] they do not account for the observed frequency dependence of $\beta$ for these compounds.[23] These studies estimate that $\beta_{1064}$ for

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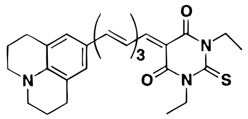
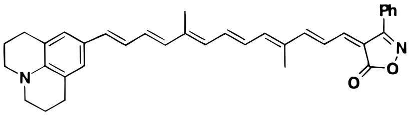
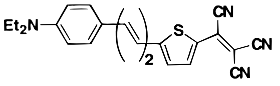
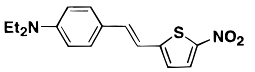
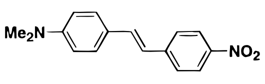
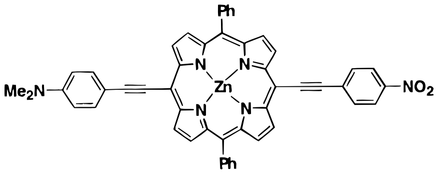
[22] Priyadarshy, S.; Therien, M. J.; Beratan, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 1504–1510.

**Table 1.** Comparative Nonlinear Optical Data for **$1(Zn^{II})$** and Selected Benchmark Organic Chromophores

| Compound | $\beta_{(\lambda)}$ ($\times 10^{-30}$ esu) | $\beta_{(o)}$ ($\times 10^{-30}$ esu) | $\mu\beta_{(o)}$ ($\times 10^{-48}$ esu) | $\left[\frac{\mu\beta_{(o)}}{(MW)}\right]$ ($\times 10^{-48}$ esu-mol/g) | Ref |
|---|---|---|---|---|---|
|  | $2169_{(1907)}$ | 911 | 8019 | 17.84 | 8 |
|  | $1781_{(1907)}$ | 849 | 13600 | 27.72 | 8 |
|  | | | 4146 | 10.75 | 26d |
|  | | | 421 | 1.39 | 26d |
|  | $73_{(1907)}$ | 55 | 363 | 1.35 | 20b, 10b |
|  | $4933_{(1064)}$ | 800 | 9840 | 12.10 | this work, 22 |

**$1(Zn^{II})$** should be approximately three- to six-fold enhanced with respect to $\beta_{(0)}$, the molecular first hyperpolarizability at zero frequency. Such a diminution of $\beta_{(0)}$ with respect to $\beta_{1064}$ may be overestimated, given that theory predicts $\beta_{830}$ to be much greater than $\beta_{1064}$, and that the mode of resonant enhancement predicted to be important for **$1(Zn^{II})$** in these calculations is not expected to be experimentally significant.[24,25] Nevertheless, a *conservatively* estimated minimal magnitude of $\beta_{(0)}$ for this chromophore of ~800 x $10^{-30}$ esu compares well with the extrapolated $\beta_{(0)}$'s for the very best organic chromophores for second harmonic generation reported to date: these molecules possess $\beta_{(0)}$'s not significantly in excess of $1000 \times 10^{-30}$ esu (Table 1).[26] As such, **$1(Zn^{II})$** represents the first metal-containing chromophore with a molecular first hyperpolarizability in this range.

Given that **$1(Zn^{II})$** is simply the prototype molecule based on our new set of design criteria for D-bridge-A compounds that possess large molecular first hyperpolarizabilities, we emphasize that (i) it is a virtual certainty that chemical modifications to the push−pull [(arylethynyl)porphinato]metal blueprint will lead to systems possessing significantly larger $\beta_{(0)}$'s, and (ii) the concepts for chromophore engineering discussed herein should find wide application in the field of nonlinear optics. Moreover, because **$1(Zn^{II})$** possesses a significant dipole moment (~12.3 D),[22] the technologically relevant parameter $\mu\beta_{(0)}$ will also be correspondingly large. Table 1 compares the molecular first hyperpolarizabilities, $\mu\beta_{(0)}$ values, as well as the quantity $\mu\beta_{(0)}$ normalized by the chromophore molecular weight of **$1(Zn^{II})$** with some of the more impressive all-organic NLO chromophores reported to date and the 4-(dimethylamino)-4′-nitro-*trans*-stilbene (DANS) standard; **$1(Zn^{II})$** ranks favorably with respect to these systems regardless of the gauge utilized for chromophore comparison. It is also worthy of note that this extrapolated $\beta_{(0)}$ value for **$1(Zn^{II})$** is more than 20-fold greater than the molecular first hyperpolarizabilities that have been evaluated for the simple diarylethynes

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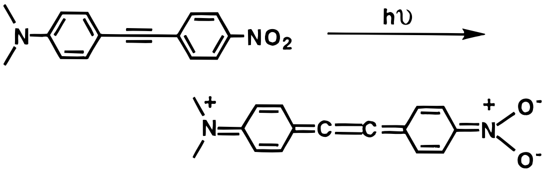
[23] These studies[22] predict that $\beta_{830}$ should be resonantly enhanced 1 order of magnitude more than $\beta_{1064}$ for **$1(Zn^{II})$**, which is not borne out by experiment.

[24] These calculations[22] predict that resonant enhancement of $\beta_{830}$ and $\beta_{1064}$ for **$1(Zn^{II})$** derives from a B (Soret) band two-photon absorption ($\lambda$ = 920 nm) process. Such a predicted degree of resonant enhancement for $\beta_{1064}$ with respect to $\beta_{(0)}$ is inconsistent with experiment: the observed quadratic dependence of I($2\omega$) on I($\omega$) (the input power) rules out any significant contribution of two-photon-derived enhancements of the HRS signal. Furthermore, two-photon resonant enhancement requires at least some oscillator strength in the transition to the virtual state that lies intermediate in energy between the ground and excited states; any significant absorption cross section for these processes would result in the production of the highly fluorescent $S_1$ excited state of these porphyrin chromophores. No stimulated emission can be detected under the conditions of these HRS experiments.

[25] A reviewer has pointed out that it is not possible to completely rule out a contribution of two-photon absorbance fluorescence photons to the signal intensity data plotted in Figures 2 and 3 (see ref 24); such two-photon absorption fluorescence has been previously shown to be a major source of photons in HRS SHG measurements (see, for example: Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1994**, *65*, 2190−2194). Two-photon fluorescence may account for the fact that theory does not model the observed frequency dependence of $\beta$ for **$1(Zn^{II})$** (see ref 22); we wish to point out however that recent EFISH measurements carried out on **$1(Zn^{II})$** at 1906 nm irradiation gives a value of $\mu\beta(0)$ consistent with that reported in Table 1 (Cai, Y.-M.; LeCours, S. M.; Therien, M. J.; Jen, K.-Y., manuscript in preparation), which is based on the HRS data reported herein.

[26] (a) Dhenaut, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; Le Bozec, H. *Nature* **1995**, *374,* 339−342. (b) Gilmour, S.; Montgomery, R. A.; Marder, S. R.; Cheng, L.-T.; Jen, A. K.-Y.; Cai, Y.; Perry, J. W.; Dalton, L. R. *Chem. Mater.* **1994**, *6,* 1603−1604. (c) Blanchard-Desce, M.; Lehn, J.-M.; Barzoukas, M.; Ledoux, I.; Zyss, J. *Chem. Phys.* **1994**, *181,* 281−289. (d) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118−1120.

(eq 4),[7] demonstrating rather eloquently the degree of enhancement in $\beta_{(0)}$ values that can be achieved when the bridge connecting D to A is polarizable and manifests a large transition moment with considerable CT character (Scheme 2).

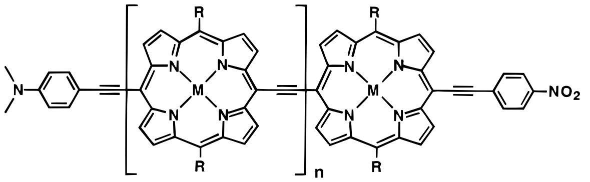


(4)

## Summary and Conclusion

Due to their exceptionally large $\beta_{830}$ and $\beta_{1064}$ values, this new class of chromophoric compounds along with those yet to be built based on the design criteria described herein, hold considerable promise for materials for second harmonic generation as well as for electrooptic devices based on the Pockels effect.[1d] Prior to their incorporation into any material or device, the origin of the different wavelength dependences of the molecular first hyperpolarizability for both **1(Zn$^{II}$)** and **1(Cu$^{II}$)** will have to be explored, as well as its potential correlation with metal electronic structure. This aside, preliminary evaluation of the thermal stability of **1(Zn$^{II}$)**, however, does indicate that this new chromophoric archetype appears to be suitable for eventual incorporation into the types of polymer matrices thought to be ideal for such electrooptical applications.[27]

Most importantly, in addition to demonstrating how the push-pull [(arylethynyl)porphinato]metal structural motif can be used as a critical design element in the fabrication of compounds that possess large molecular first hyperpolarizabilities, we wish to stress that such systems offer a number of obvious advantages over the vast landscape of compounds and materials for second harmonic generation that have employed more typical unsaturated organic structures to bridge an electron donor and acceptor. Firstly, push−pull [(arylethynyl)porphinato]metal structures enable the alignment of the massive porphyrin transition dipole along the molecular charge-transfer axis; furthermore, as indicated in eq 5, the magnitude of this transition dipole can be readily modified.



(5)

Secondly, such systems feature relatively small transition energies between the ground and excited states; moreover, when the molecular bridge linking the electron-releasing and electron-accepting groups is based on porphyrin or similar chromophores, this parameter can be readily fine tuned. Thirdly, relative to traditional materials for second harmonic generation based on donor−acceptor polyenes or low band gap conducting polymers,[5,8−10,28] in which the alteration of the contribution of the charge-separated form to the ground state structure has relied chiefly on D−A modification, assemblies such as these allow (i) exploration of the role played by metal electronic structure (transition metal size, spin multiplicity, oxidation state) in determining the dimension of the molecular first hyperpolarizability; (ii) modulation of chromophore electronic properties through axial ligand variation at the (porphinato)metal center, potentially providing precise and subtle regulation of molecular optoelectronic properties as well as a new mode of covalent attachment of chromophores to a polymer backbone; and (iii) amplification of chromophore polarizability through the engineering of metal-to-metal or macrocycle-to-macrocycle charge transfer character along the D-to-A molecular axis. Such ease of electronic modification of an extremely potent NLO chromophore for second harmonic generation is unusual as well as advantageous; it strongly suggests that the present large molecular first hyperpolarizability exhibited by **1(Zn$^{II}$)** will soon be surpassed by other compounds and materials based on the push−pull [(arylethynyl)porphinato]metal structural motif.

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[27] (a) Preliminary TGA studies of **1(Zn$^{II}$)** indicates that 1% of the mass is lost over a 160−300 °C temperature range. Mass spectral analysis of the vapor shows fragments of 72 and 44 atomic mass units (amu). While the peak at 72 amu may correspond to loss of residual tetrahydrofuran, the 44 amu peak may derive from dealkylation of the amino functionality. As Moylan has pointed out (*J. Am. Chem. Soc.* **1993**, *115*, 12599−12600), the electron-releasing dialkylamino moieties are generally the least stable entities in push−pull chromophores that feature these groups; replacing the dialkylamino functionality with a diphenylamino group typically increases the $T_d$ of an NLO chromophore in excess of 50 °C without any appreciable alteration of the molecule's first hyperpolarizability; such a simple change of functionality would move our chromophores well within the >200 °C thermal stability range thought to be crucial for optoelectronic device applications. In any event, the 1% mass loss is too small to correlate with any uniform decomposition process and may in fact derive from chemical reactions occurring at the surface of the material. The next decomposition process occurs over a 340−420 °C temperature domain and coincides with an additional 6% mass loss and shows a number of fragments of varying molecular weight in the mass spectrum. (b) More relevant to the suitability of these new chromophoric systems to the development of nonlinear materials is their stability in poled organic films. An optical quality, guest−host NLO chromophore−polyimide thin film was prepared by imidization of a 12 weight % solution of **1(Zn$^{II}$)** in polyamic acid [Ultradel 4212 (AMOCO)] at 220 °C using standard methods. Isothermal heating of this film at 250 ˚C for 30 min showed no changes in the optical spectrum of the chromophore guest; further heating of the film at 275 °C for an identical period of time showed a minor (<5%) decrease in the B- and Q-band absorption intensities of the **1(Zn$^{II}$)** guest. While it is clear that **1(Zn$^{II}$)** exhibits remarkable thermal stability in a polyimide host, it is an open question at this time whether this small loss in optical intensity observed at 275 °C derives from a decomposition process or sublimation of the chromophore. (Cai, Y.-M.; LeCours, S. M.; Therien, M. J.; Jen, K.-Y., manuscript in preparation.)

[28] (a) Bredas, J. L. *Synth. Methods* **1987**, *17,* 115−121. (b) Brédas, J. L.; Dory, M.; Thémans, B.; Delhalle, J.; André, J. M. *Synth. Methods* **1989**, *28,* D533−D542.