Large Molecular Hyperpolarizabilities in “Push−Pull” Porphyrins. Molecular Planarity and Auxiliary Donor−Acceptor Effects

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Linear optical and SHG coefficients of a number of “push−pull” porphyrins are analyzed using the semiempirical INDO/S Hamiltonian and singles-only CI. The NLO response properties are computed at a nonresonant excitation energy of 0.1 eV using the correction vector formalism, and the calculations are carried out in both ideal planar and SYBYL force-field optimized geometries. The results strongly suggest that large NLO responses may be obtained by (1) minimizing the dihedral twist of phenyl substituents with respect to the porphyrin plane, (2) replacing the homoaromatic phenyl rings in tetraphenylporphyrins by electron excessive or deficient heteroaromatic rings such as pyrrole or tetrazine, (3) exploiting the electron-excessive and -deficient sites of the porphyrin π-electron bridge itself. Thus, functionalizing the electron excessive β position with donor substituents and electron-deficient meso position with acceptor substituents leads to enhanced NLO response properties. The enhancement in the NLO response properties is modest in chromophores containing spacer groups which reduce the dihedral twist angles. This is attributed to the diminished inductive effect of the electron excessivity/deficiency of the porphyrin rings due to the intervening spacer and phenyl moieties.

I. Introduction

A wide variety of organic π-conjugated molecules have been scrutinized both theoretically and experimentally for large optical nonlinearities.[1−7] The outcome of these studies is the demonstration that organic molecules with extended π-conjugated bridges functionalized with strong electron donors and acceptors can exhibit extremely large second-order optical nonlinearities. Substantial research has also been directed toward converting these large molecular optical nonlinearities to large bulk optical nonlinearities for use in photonic device technologies.[3c,d] These studies have also demonstrated the attractive properties of organic materials compared to conventional inorganic materials such as $LiNbO_3$, KH_2PO_4, and $KTiOPO_4$, even though the latter are currently the materials of choice in device applications.[5] One important attraction of organic materials over conventional inorganic materials is tailorability. This is because the bulk NLO response of these materials can largely be accounted for from the contributions of the molecular constituents, making it straightforward to design new materials with optimal optical properties.

To date the most effective molecular chromophoric architectures have been quasi-one-dimensional π-conjugated organic molecules endcapped with strong donor and strong acceptor substituents.[6,7] Chromophores that vary in the strength/number of the donor and acceptor groups and in conjugation length have been designed, synthesized, and characterized. A simple two-level model[8] (eq 1), derived from a more general perturbation expression for the first hyperpolarizability, has provided

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a useful guideline for designing new NLO chromophores.

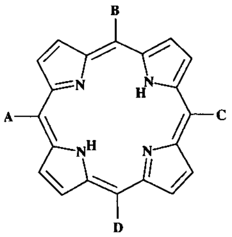
$$\beta_{\text{two-level}} = \frac{3e^2}{2\hbar^3}\frac{\omega_{ge} f_{ge}\Delta\mu_{ge}}{[\omega_{ge}{}^2-\omega^2][\omega_{ge}{}^2-4\omega^2]} \qquad (1)$$

According to this model, the first hyperpolarizability depends on the optical transition energy ($\hbar\omega_{ge}$), the associated oscillator strength (f_{ge}), and the difference between the ground- and excited-state dipole moments ($\Delta\mu_{ge}$). While variation in the strengths of donor and acceptor substituents modulates $\Delta\mu$ and the oscillator strength, the expanse of the π-conjugation most affects the optical transition energy. Thus, increasing the length of the conjugated bridge and/or the strength of the donor or acceptor groups enhances the NLO response properties. This has prompted a search for new extended π-conjugated bridges that can be functionalized with strong donor and acceptor groups. These studies have demonstrated that extended push–pull polyenes, polyphenyls, polyynes, cumulenes, or a combination of these bridges, functionalized with suitable strong electron donors and acceptors, exhibit large NLO responses.[6,7] A disadvantage of such extended quasi-one-dimensional chromophores is that the increase in NLO response is usually accompanied by bathochromic shifts in the intramolecular charge-transfer excitations, eroding the chromophore transparency in the visible region—an unacceptable property for many photonic applications. Also, as the molecular conjugation length increases, the thermal stability generally diminishes.[9,10]

While most of the organic chromophores studied to date are quasi-one-dimensional in architecture, there have been attempts to design two-dimensional chromophores based on large macrocyclic structures such as porphyrins,[11] metalloporphyrins,[12,13] and metallophthalocyanines.[14] The early theoretical prediction by Li et al. that substituted phthalocyanines could exhibit large SHG coefficients[14] was later confirmed experimentally for porphyrins by Suslick, et al. (Chart 1). Recent experimental work of LeCours et al.[12a,b] shows that metalloporphyrin complexes with intervening alkenyl or alkynyl links exhibit large NLO response. This has also been theoretically confirmed by Priyadarshy et al.[12b] Furthermore "push–pull" porphyrin chromophores have been successfully incorporated into Langmuir–Blodgett films that exhibit substantial bulk NLO responses.[11a]

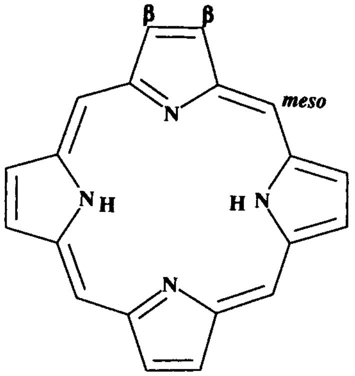
Although the porphyrin-based chromophores examined to date exhibit large NLO responses, the NLO response of these chromophores is actually relatively small considering the large number of π-electrons in the system. Suslick et al. ascribed the modest response of these donor–acceptor porphyrins to two possible effects.[11b] First, there is a competitive charge transfer, in multiply substituted porphyrins (such as chromophore **Id** in Chart 1), in the parallel and perpendicular directions with respect to the dipole moment, thereby reducing the EFISH response. Second, the substantial dihedral twist with respect to the porphyrin plane of the donor- and acceptor-functionalized peripheral phenyl rings, reduces effective conjugation with the porphyrin core and hence the effective charge transfer. This leads to reduced NLO response. The average dihedral twist angle between phenyl rings and the porphyrin plane in similar chromophores has been determined from X-ray crystallographic structures to be ~60°.[15] In this paper, we examine these architecture-response issues and show theoretically that push–pull porphyrins with substantial NLO response can be designed.

Chart 1



	A	B	C	D
Ia	*p*-NH$_2$-Ph	H	*p*-NO$_2$-Ph	H
Ib	*p*-NH$_2$-Ph	*p*-NH$_2$-Ph	*p*-NH$_2$-Ph	*p*-NO$_2$-Ph
Ic	*p*-NH$_2$-Ph	*p*-NO$_2$-Ph	*p*-NO$_2$-Ph	*p*-NO$_2$-Ph
Id	*p*-NH$_2$-Ph	*p*-NH$_2$-Ph	*p*-NO$_2$-Ph	*p*-NO$_2$-Ph

Chart 2



Of the two problems cited above, a possible scheme to minimize the effects of phenyl ring dihedral twisting in metalloporphyrins was suggested by LeCours et al.[12a] and by Priyadarshy et al.[12b] In these schemes, loss of conjugation via dihedral twisting is reduced by introducing intervening alkenyl or alkynyl spacer groups. The solution to the first problem, however, is much less straigthforward. In the chromophores studied by Suslick et al., the donor and acceptor substituents are attached to phenyl rings which in turn are appended to the porphyrin core at the meso positions (the β and meso positional nomenclature is shown in Chart 2). Their

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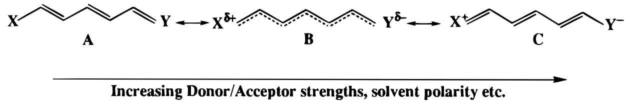
study shows that the largest NLO response is obtained by introducing two donor and two acceptor groups (chromophore **Id** in Chart 1) rather than three donors and one acceptor (**Ib**) or three acceptors and one donor (**Ic**). Such a substitution pattern leads to two mutually orthogonal separate charge transfers and hence to reduced EFISH coefficients. If, however, donor groups were introduced at the appropriate β positions and acceptor groups at the meso positions, or vice versa, there would be only one net charge-transfer direction, and thus the possibility of enhanced response. In this paper, the above two strategies, namely using spacer groups to reduce the dihedral twist angle and a modified substitution pattern, are employed to formulate new generations of push–pull porphyrins having much larger NLO response properties than existing structures. Furthermore, our recent studies[16] of electron excessivity effects on NLO response in heterocycles revealed that substantially larger NLO response properties can be obtained when the donor groups are appended to electron-excessive centers and the acceptors to electron-deficient centers. These electron-excessivity and -deficiency effects on NLO response should, in principle, be exploitable in two ways in porphyrinic chromophores: (1) by appropriately replacing the homocyclic phenyl substituents of tetraphenyl porphyrins with electron-excessive or -deficient heterocycles, (2) by identifying porphyrin electron-excessive and -deficient centers and appending electron donors to the electron-excessive centers and acceptors to the electron-deficient centers.

In this contribution, we initially discuss electron-excessive and -deficient centers in the porphyrin molecule. Then, from a wide variety of substitution patterns, we demonstrate that a very large NLO response should be attainable by exploiting the electron-excessivity and -deficiency properties of the porphyrin macrocycle. In these chromophores, we also examine the effect of the phenyl ring dihedral twist angle to which the donor and acceptor groups are attached. The phenyl ring dihedral twisting effects can be reduced using spacer fragments, thus resulting in enhanced NLO response. Properties are computed using the reliable semiempirical INDO/S Hamiltonian[17] as implemented in the ZINDO package, and NLO response properties are computed using the correction vector approach. In the next section, electron-excessivity and -deficiency principles will be briefly introduced. In section III we present the results of our calculations and analyze porphyrin hyperpolarizability at the molecular level using electron excessivity and deficiency ideas.

II. Computational Details

Electron Excessivity and Deficiency in Heterocyclic Rings. The ground-state bridge geometry of an archetypical chromophore can be distorted from a polyene-like geometry (**A**) to a cyanine-like geometry (**B**) to a polymethine-like geometry (**C**) depending on the strength of the donor/acceptor substituents and/or on the polarity of the solvent. This variation in the geometry leads to dramatic variations in the response properties of organic chromophores. Such variations are well documented and have been extensively discussed by Marder et al.[18] These studies have demonstrated that the optimal geometry yielding large response properties lies between the polyene-like (**A**) and the cyanine-like (**B**) geometries.[18] This behavior can be understood from the two-level model (eq 1). From the two-level model, it can be seen that in order to obtain large SHG coefficients, chromophores must have large oscillator strengths, small transition energies, and large changes in dipole moments between the ground and the excited states. It can be shown that the excitation energy and the transition moment are optimal (smallest excitation energy and largest oscillator strengths) when the geometry is cyanine-like. However, the change in dipole moments ($\Delta\mu$) is largest when the ground-state geometry is polyene-like **A** and the charge-transfer state geometry is polymethine-like (**C**) and is minimal at the cyanine limit.[18] Thus, the optimal geometry yielding large response properties is a compromise between these two opposing factors and hence should lie between the polyene-like and the cyanine-like geometries (the geometry between the cyanine-like and the polymethine-like would also be favorable, except that the response properties will be reversed in sign). In other words, the ground-state polarization toward the cyanine limit must be minimized to obtain a high-β chromophore. One way to minimize this ground-state polarization is by interposing an electron-rich moiety between the donor and the bridge and an electron-deficient moiety between the acceptor and the bridge. The electron-rich moiety should effectively screen the depletion of electron density on the donor and hence reduce the ground-state polarization, thereby increasing the effective strength of the donor substituent. The electron-deficient moiety would serve a similar function with respect to the acceptor.



Heterocyclic rings, depending on the number of π-electrons, π-orbitals, and the heteroatom electronegativity, can be classified as electron excessive or electron deficient.[16,19,20] For example, pyrrole, a typical aromatic five-membered ring with six π-electrons and five π-orbitals, is an electron-excessive π-system, due to excess electron density on the ring carbon atoms. Similarly, pyridine with six π-electrons and six π-orbit-

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(20) Electron excessivity and deficiency are defined as the actual electron density on the carbon atoms of the heterocycle minus the number of π-electrons formally donated by the carbon atoms to the π-framework.[16]

als, is an electron-deficient system due to the deficiency of electron density on the ring carbon atoms. Recent studies[16] show that the electron excessive/deficient heterocycles effectively screen the ground-state polarization in simple stilbene-based chromophores and hence increase substituent donor/acceptor capability. This increased donor/acceptor capability increases the NLO response properties of chromophores in which donor groups are appended to electron-excessive centers and acceptor groups to electron-deficient centers. The electron excessivity/deficiency of the heterocyclic rings has been used, both theoretically and experimentally, to design new generations of chromophores exhibiting large NLO response properties.[16,21]

In designing optimal porphyrinic NLO chromophores, the electron-excessivity principle can be employed in two ways. First, it can identify suitable substitution patterns on the porphyrin skeleton itself, such as appending donor substituents to electron-excessive sites and acceptor substituents to deficient sites. Second, the phenyl rings to which the donor and acceptor groups are attached can be replaced by electron excessive/deficient heterocyles. To investigate the first effect, the electron-excessive and -deficient centers of the porphyrin skeleton must first be identified. In porphyrins, two possible conjugation pathways have been proposed based on aromatic ring current and bond distance data.[15,22−25] One is an *inner* 18-electron, 16-orbital subfragment (a structure similar to [16]annulene; Figure 1a) and the other is an *outer* 18-electron, 18-orbital subfragment (an [18]annulene-like structure; Figure 1b). While there have been [17]annulene-like structures proposed in the literature,[26] they contribute minimally to the electronic structure properties of porphyrins. A number of electronic structure calculations,[22] X-ray crystallographic,[15,24] and aromatic ring current studies[25] support both the [16]annulene and [18]annulene structures as the predominant porphyrin conjugative pathways.[23] The [16]annulene-like structure is a π-excessive subfragment, and the [18]annulene-like structure is a π-deficient subfragment. Analysis of the electron density on the various carbon atoms of the two subfragments shows that in both the cases, the meso positions are electron deficient and the β positions are electron-excessive (labeling is shown in Figure 1). Note that the β labeling in Figure 1a is different from the formal β labeling of the porphyrin skeleton itself. We chose to designate the electron-excessive center in this fragment as the β-carbon atom. Thus, attaching donor groups to the π-excessive β positions and acceptors to the π-deficient meso positions should afford larger NLO response properties than appending both donor and acceptor groups to the electron-deficient meso positions. In the second scheme, we replace the phenyl rings by electron-excessive pyrrole rings at the donor portion and by the electron-deficient tetrazine ring at the acceptor portion. For all these chromophores, the SHG coefficients in the both SYBYL force field[27] optimized geometry and in the enforced planar geometry are computed using the correction vector approach, described in detail elsewhere.[28]

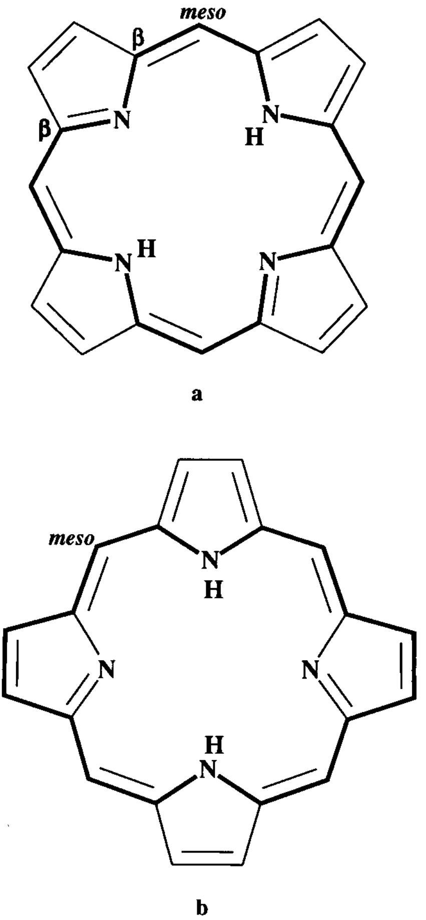

Figure 1. The inner and outer aromatic subfragments of the porphyrin skeleton. The bold lines in **a** and **b** represent the inner and outer aromatic subfragments, respectively. The labeling of the carbon atoms as β and meso are shown. Note that the β-position of the [16]annulene-like subfragment (**a**) is different from the porphyrin skeletal nomenclature which is used in **b**.

III. Results and Discussion

(A) Aromatic Fragment Behavior. We begin by analyzing the behavior of the porphyrin subfragments upon substitution and excitation; actual molecules are discussed in Section III.B. The molecules are placed in

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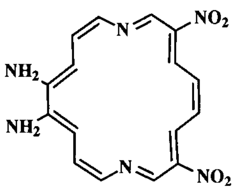
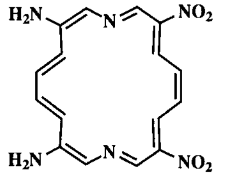
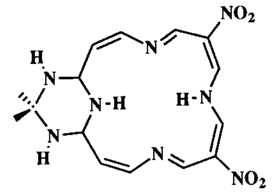
Table 1. Linear and NLO Response Properties of Chromophore Set II at an Excitation Energy of 0.1 eV for SYBYL Force-Field Optimized and Enforced Planar Geometries



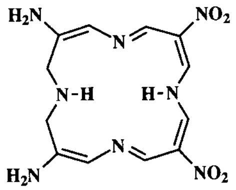
IIa



IIb



IIc



IId

	λ_{max} (nm)		$\Delta\mu$ (debye)		β_x (10^{-30} esu)		$\mu\beta$ (10^{-48} esu)	
chromophore	optimized	planar	optimized	planar	optimized	planar	optimized	planar
IIa	490.7	519.1	10.17	8.04	31.59	54.16	637.8	1065.8
IIb	389.5	431.6	15.67	4.06	28.56	37.90	531.3	679.3
IIc	1079.2	*a*	23.34	*a*	614.83	*a*	7545.2	*a*
IId	419.1	403.5	3.43	14.87	24.36	52.61	266.3	839.3

[a] Since the SYBYL optimized geometry of chromophore **IIc** is essentially planar, the response properties were not computed in the enforced planar geometry.

the $X-Y$ plane, with X being the polar axis. The NLO response of four chromophores are analyzed (chromophore set **II**; Table 1) in which donor and acceptor substituents are appended to the electron-deficient and excessive centers in the two subfragments. In molecules **IIa** and **IIc**, donor substituents (NH_2) are attached to the electron-excessive β-carbon atoms and the acceptor substituents (NO_2) to the electron-deficient meso carbon atoms. In **IIa**, the bridge is an [18]annulene-like subfragment, and in **IIc**, it is an [16]annulene-like subfragment. In **IIb** and **IId**, both the donor and acceptor substituents are appended to the electron-deficient meso carbon atoms. The bridges in **IIb** and **IId** are [18]annulene-like and [16]annulene-like subfragments, respectively. In **IIc**, a methylene fragment links the two amino groups to avoid out-of-plane twisting of the two substituents. Note that although the NLO response of **IIc** might be expected to be somewhat larger than for the other chromophores of set **II** due to the enhanced donor capacity of a secondary amine versus a primary amine,[6] this enhancement should not be very large. It must also be emphasized that in **IIc** the bridge carbon atoms C1 and C15 are sp^2 hybridized, and each has an unpaired electron.[33] Thus, **IIc** is better described as a biradical. While it is not known at this point if **IIc** would have a ground-state singlet or triplet electronic structure, an initial single SCF energy calculation of the singlet and triplet states indicates that the singlet is more stable that the triplet by about 5 kcal/mol. The linear and NLO response properties of these chromophores are presented in Table 1. Since the full SYBYL optimized geometry of **IIc** is nearly planar, the NLO response properties are computed only in the full SYBYL optimized geometry. Note that functionalizing the electron-excessive β-carbon atoms with donor groups and the electron-deficient meso-carbon atoms with acceptor groups effects significant enhancement of β values in **IIa** and **IIc** compared to those in **IIb** and **IId**.

The exceptionally large hyperpolarizability of **IIc** requires additional analysis. To understand this large response, the evolution of the **IIc** SHG coefficient as excited states are added in the SOS expression is plotted in Figure 2. Note that there is a large contribution from the second state and small contributions from higher excited states. An examination of the excitation energies and the change in dipole moments of these states (Table 1) shows that for the first excited state, a strong transition ($f = 0.22$) accompanied by a large change in dipole moment and a very small excitation energy makes a large contribution to the SHG coefficient. The dominantly allowed state (state 10; $f = 1.41$) has a small $\Delta\mu$ and a larger excitation energy and contributes marginally to the SHG coefficient. Thus, the large NLO

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(33) Molecules **IIc** and **IId** are in fact biradicals since C1 and C15 are assumed to be sp^2 hybridized. This assumption is necessary to maintain the conjugation from donor to acceptor. Note however that there are two possible biradical resonance structures for both **IIc** and **IId**. For example, in the case of **IIc**, one can draw a resonance structure in which bonds C6−C7 and C9−C10 are double, in which case C1 and C15 would have unpaired electrons, and another structure in which bonds C1−C2 and C14−C15 are double, in which case C7 and C9 would have unpaired electrons. If both canonical forms contribute equally then the initial assumption that C1 and C15 are sp^2 hybridized is correct. In our calculations we have chosen the former resonance structure for the SYBYL optimization.

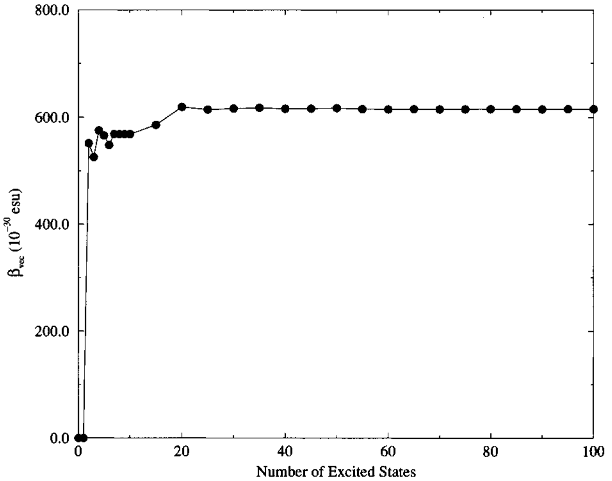


Figure 2. Evolution of the vector component of the SHG coefficient of molecule **IIc** as excited states are added in the SOS expression.

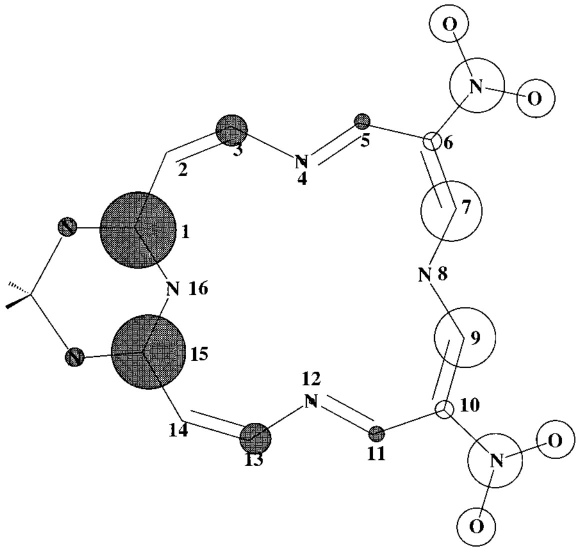


Figure 3. INDO/S computed difference in charge densities of the ground and first excited state of chromophore **IIc**. The circles are scaled according to the magnitude of the charge density difference. Black circles represent negative charge densities (depletion), and white circles represent positive charge densities (accumulation). The numbering of the bridge is also given.

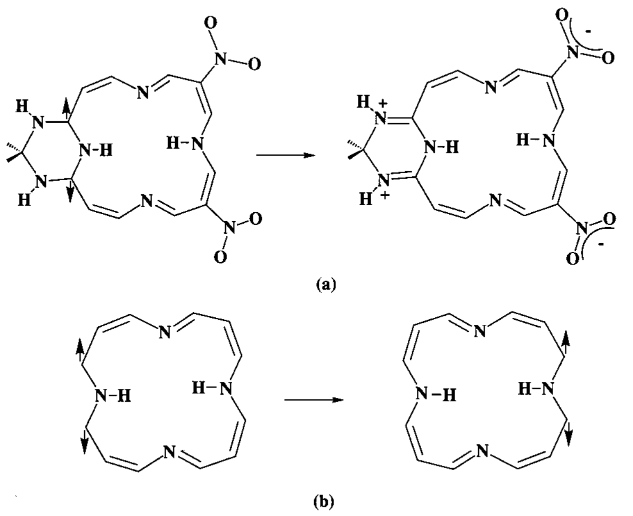


Figure 4. Schematic representation of the charge-transfer excitations in molecule **IIc**. The charge transfer from donor to acceptor substituents is shown in (a). The other near degenerate transition within the bridge is shown in (b). The arrows indicate the unpaired electron spins.

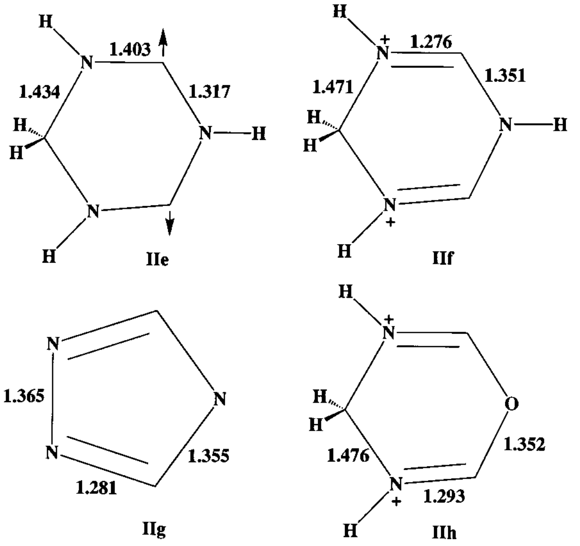
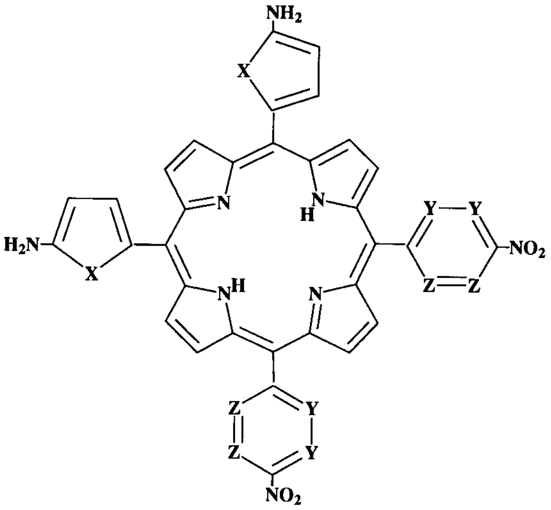


Figure 5. 6-31G** optimized bond lengths of molecular structures **IIe**–**g**. The arrows indicate unpaired spins at atoms C2 and C6. Since these are sp^2-hybridzed carbon atoms, each possesses an unpaired electron. The X-ray diffraction-derived metrical parameters of a related diprotonated oxadiazine (**IIh**) from ref 33 are shown for comparison. See text for details.

response of **IIc** is attributable predominantly to the very small excitation energy of the first excited state.

To understand the origin of the very small excitation energy of chromophore **IIc**, the INDO/S computed difference in charge densities between the ground and first excited state are plotted (Figure 3). The plot shows a large intramolecular charge transfer from carbon atoms 1 and 15 to carbon atoms 7 and 9 in addition to charge transfer from the donor to the acceptor substituents, indicating that this transition is composed of two subtransitions. These are an intramolecular charge transfer between the donor and acceptor groups and a near-degenerate transition within the bridge. The excited state in the former transition is possibly homoaromatically stabilized[30] as in the 3,5-diprotonated 1,4-dihydro-*s*-triazine **IIf** (Figure 4). This transition is shown pictorially in Figure 5a. It has been generally found that aromatic systems retain the aromatic stabilization even when the π-conjugation is ruptured, and one or more intervening groups, specifically CH_2 groups, are inserted. This unusual stabilization is termed homoaromaticity.[30] While homoaromaticity in homocyclic ring structures is well-known, it is much less common in heterocyclic rings such as these. To better understand the unusual homoaromaticity of **IIf**, a full optimization of the 1,3,4,5-tetrahydro-*s*-triazine biradical (**IIe**) and 3,5-diprotonated 1,4-dihydro-*s*-triazine (**IIf**), which are structurally similar to the ground- and charge-transfer states of the donor fragment of **IIc**, respectively, were carried out using a 6-31G** basis set.[31] The optimized geometries of **IIe** and **IIf** are shown in Figure 4. The 6-31G** optimized geometry of 1,3,5-triazole (**IIg**) is also given in Figure 4 for comparison. The optimized geometry of **IIf** clearly reveals the triazole-like geometry. The close agreement between the various bond lengths in **IIf** and **IIg**

Table 2. Linear and NLO Response Properties of Chromophore Set III at an Excitation Energy of 0.1 eV for SYBYL Force-Field Optimized and Planar Geometries



III

chromophore	X	Y	Z
IIIa	CH=CH	N	CH
IIIb	CH=CH	N	N
IIIc	O	CH	CH
IIId	O	N	CH
IIIe	O	N	N
IIIf	S	CH	CH
IIIg	S	N	CH
IIIh	S	N	N
IIIi	NH	CH	CH
IIIj	NH	N	CH
IIIk	NH	N	N

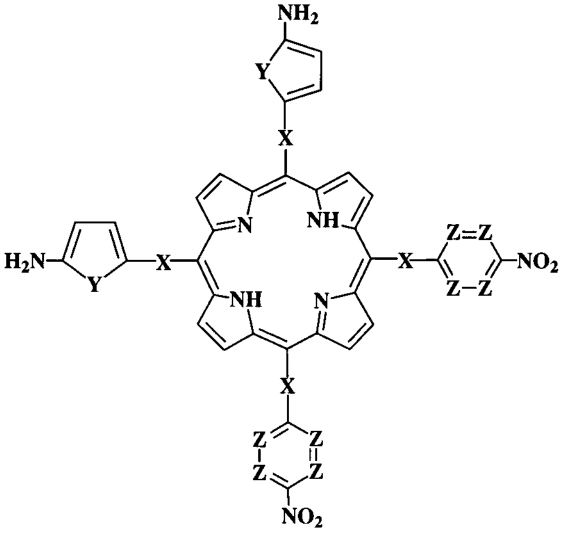
	λ_{max} (nm)		$\Delta\mu$ (debye)		β_x (10^{-30} esu)		$\mu\beta$ (10^{-48} esu)	
chromophore	optimized	planar	optimized	planar	optimized	planar	optimized	planar
Ia	359.0	399.0	5.08	17.66	64.74	117.66	554.1	1222.2
Ib	358.8	422.0	3.75	18.62	35.41 (<10)[a]	120.57	330.59	1354.0
Ic	382.8	416.3	20.91	10.86	49.24 (20 ± 10)[a]	118.16	438.35	1202.04
Id	358.9	423.2	6.45	14.75	43.39 (30 ± 10)[a]	124.17	747.8	2496.0
IIIa	362.6	438.7	7.54	20.10	64.02	137.92	687.76	1446.80
IIIb	446.3	462.0	23.67	19.21	78.93	174.65	1349.74	3404.8
IIIc	412.4	440.0	24.43	12.32	75.55	186.85	908.32	3237.28
IIId	417.1	459.3	14.87	19.39	87.68	219.27	942.84	2067.71
IIIe	448.2	473.0	25.08	15.54	85.02	232.08	1222.98	4048.29
IIIf	391.0	436.5	16.12	12.46	46.42	174.74	838.73	3189.91
IIIg	359.7	456.5	7.51	19.25	59.44	204.25	1042.33	2058.34
IIIh	450.5	471.2	24.79	15.94	69.35	223.88	1352.37	4062.90
IIIi	411.3	451.6	22.14	13.83	80.43	175.29	839.91	3387.10
IIIj	431.4	460.3	25.18	16.49	89.19	189.95	742.33	1813.41
IIIk	448.0	478.6	24.59	16.41	93.14	227.99	1071.33	4470.5

[a] Experimental values for $CHCl_3$ solutions in parentheses from ref 11b. The experimental excitation energy was 0.65 eV.

therefore supports the homoaromatic character of **IIf** and hence of the donor segment of the **IIc** excited state. Further support for the homoaromatic stabilization of **IIf** comes from the recent crystal structure of an architecturally similar protonated oxadiazine (**IIh**).[32] The intramolecular transition within the bridge of chromophore **IIc** can therefore be explained as follows. As mentioned earlier, atoms C1 and C15 are sp^2 hybridzed and each has an unpaired electron.[33] Upon excitation, the unpaired electrons on atoms C1 and C15 are transferred to atoms C7 and C9. This transition is degenerate in the unsubstituted [16]annulene-like bridge because the ground and excited states in this transition are simply the two degenerate resonance structures of the bridge. A pictorial representation of this transition is shown in Figure 5b. This degeneracy is lifted only marginally on substitution with donor and acceptor groups. This transition involves a large change in charge density at atoms C1, C7, C9, and C15. Thus, substantial homoaromatic stabilization of the charge-separated species accompanied by a near-degenerate transition within the bridge in the first excited state of **IIc** leads to a small excitation energy and hence to a large NLO response.

(B) Porphyrinic Chromophores. Table 1 shows that chromophores in which strong donor substituents are appended to electron-excessive β-carbon atoms and strong electron-acceptor substituents to electron-deficient meso carbon atoms exhibit substantially larger NLO response properties than chromophores in which

Table 3. Linear and NLO Response Properties of Chromophore Set IV at an Excitation Energy of 0.1 eV for SYBYL Force-Field Optimized and Planar Geometries



IV

chromophore	X	Y	Z
IVa	C≡C	CH=CH	CH
IVb	N=N	CH=CH	CH
IVc	N=N	NH	N

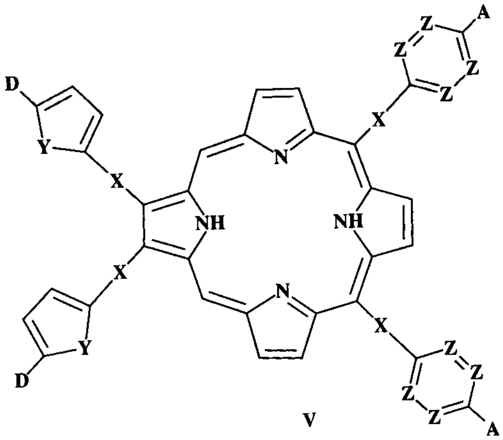
	λ_{max} (nm)		$\Delta\mu$ (debye)		β_x (10^{-30} esu)		$\mu\beta$ (10^{-48} esu)	
chromophore	optimized	planar	optimized	planar	optimized	planar	optimized	planar
IVa	416.7	416.9	18.27	18.25	146.75	146.76	2633.8	2636.2
IVb	539.3	539.0	9.30	9.35	193.96	206.31	5454.7	5654.9
IVc	552.4	566.9	14.86	12.14	245.49	326.67	5892.8	10122.0

both donors and acceptors are appended to the electron-deficient meso carbon atoms. To explore the above idea further, the NLO response of a number of porphyrinic chromophores with sequentially varied architectures (chromophore sets **III**, **IV**, and **V**, Tables 2−4, respectively) were investigated. The NLO responses were calculated in both planar and SYBYL force-field optimized geometries to examine the effect of the donor/acceptor substituted aromatic ring dihedral twist. In chromophore sets **III** and **IV**, both the donor (NH_2) and the acceptor (NO_2) substituents are attached to the electron-deficient porphyrin meso-carbon atoms, and in chromophore set **V** (chromophores **Va**, **Vb**, and **Vc**) the donor substituents are attached to the electron-rich porphyrin β-carbon atoms and the acceptors to the electron-deficient meso-carbon atoms. The SHG coefficients of chromophores having a reversed substitution pattern (chromophores **Vd**, **Ve**, and **Vf**) were also computed, to examine the effect of the electron excessivity/deficiency of the porphyrin bridge. The NLO response of additional chromophores in which the phenyl rings are replaced by auxiliary donors, such as pyrrole, and auxiliary acceptors, such as tetrazine, were also computed to examine the auxiliary donor and acceptor effects of the peripheral phenyl rings on the NLO response properties. The INDO/S computed NLO responses of these chromophore sets are presented in Tables 2−4. Available experimental SHG coefficients of several of the chromophores (chromophore set **I**) in $CHCl_3$ solution at an excitation energy of 0.65 eV are also presented in Table 2 for comparison.

Comparison across chromophore set **III** (Table 2) shows that the experimental SHG coefficients are invariably somewhat smaller than the theoretical values. These differences may well arise from phenyl group dihedral twist angles. The angular twisting will lead to loss of conjugation and diminished NLO response. The drastic reduction in response of these chromophores between the planar idealized and optimized geometries, evident from Table 2, clearly demonstrates this effect. Typical effects on β_x of changing the dihedral twist angle vary from ~85% in **Ia** to ~240% in **Ib**. The larger SHG coefficient of chromophore **Ia** in the optimized geometry compared to those of **Ib−d** is surprising. Also, the variation of the SHG coefficients of **Ia−d** in the planar geometry is minimal. This suggests that there are two independent charge-transfer processes between the pairs of donor and acceptor groups. Additional support for this speculation is obtained from the $\mu\beta$ value of **Id**, which is ~2× that of **Ia**. This finding also supports the conjecture of Suslick et al.[11] regarding the smaller NLO response properties of **Ib−d**, i.e., that there are two independent charge transfers in these chromophores and that these occur in perpendicular directions, resulting in smaller EFISH coefficients.

Electron excessivity/deficiency effects of heteroaromatic rings on NLO response in chromophore set **III** can be discerned in the response properties of chromophores **IIIa−k** (Table 2). Replacing a homocyclic benzene ring by an electron-deficient moiety such as diazene or tetrazine or an electron-excessive moiety such

Table 4. Linear and NLO Response Properties of Chromophore Set V at an Excitation Energy of 0.1 eV for SYBYL Force-Field Optimized and Planar Geometries



V

chromophore	D	A	X	Y	Z
Va	NH_2	NO_2	C≡C	CH=CH	CH
Vb	NH_2	NO_2	N=N	CH=CH	CH
Vc	NH_2	NO_2	N=N	NH	N
Vd	NO_2	NH_2	C≡C	CH=CH	CH
Ve	NO_2	NH_2	N=N	CH=CH	CH
Vf	NO_2	NH_2	N=N	NH	N

	λ_{max} (nm)		$\Delta\mu$ (debye)		β_x (10^{-30} esu)		$\mu\beta$ (10^{-48} esu)	
chromophore	optimized	planar	optimized	planar	optimized	planar	optimized	planar
Va	403.5	405.5	13.04	12.94	157.22	156.61	2492.4	2395.2
Vb	477.4	477.7	4.33	4.31	218.76	259.72	4625.4	4633.6
Vc	489.7	492.6	12.77	13.11	345.75	493.50	3616.78	6443.74
Vd	402.1	*a*	9.09	*a*	98.86	*a*	2390.65	*a*
Ve	530.9	*a*	5.63	*a*	352.69	*a*	6435.4	*a*
Vf	537.6	*a*	10.02	*a*	305.22	*a*	8897.73	*a*

[a] The NLO responses of these chromophores were not computed in the enforced planar geometries.

as thiophene or pyrrole leads to an increased SHG coefficient. Thus, replacing the benzene rings at the donor end by electron-excessive pyrrole rings and the benzene rings at the acceptor end by electron-deficient tetrazine rings (**Id** → **IIIk**) leads to ~2-fold increase in both β_{vec} and $\mu\beta$.

The linear optical and SHG coefficients of chromophore set **IV** (Table 3) show that extremely large NLO responses in push–pull porphyrins can be obtained by reducing the dihedral twist of the phenyl rings. The very minimal variation in the linear and NLO properties of chromophores **IVa** and **IVb** between the planar and SYBYL optimized geometries suggests that the intervening spacer groups such as azo or acetylenic bridges reduce the dihedral twisting effects of the phenyl rings. The dihedral twist angles in the SYBYL optimized geometries of **IVa** and **IVb** are found to be 7° and 0.5°, respectively. While both the azo and acetylenic spacer groups reduce the dihedral twisting effects of the phenyl rings, the former leads to smaller dihedral twist angles and larger SHG coefficients than the latter. The much greater response of chromophore **IVc** compared to those of **IVa** and **IVb** demonstrates that introducing auxiliary donor and acceptor groups increases the NLO response. Indeed, the SHG coefficients of these chromophores are at least an order of magnitude larger than the NLO response properties of the majority of push–pull porphyrins found in the literature (**Ib**–**d**).

While the SHG coefficients of chromophore set **V** are in general larger than those of set **IV**, the net $\mu\beta$'s of set **V** members can be smaller (see Tables 3 and 4) because, while there are two equivalent charge transfers in chromophore set **IV** (the β_x and β_y are very similar in magnitude), there is only one net charge transfer in set **V**. Note however that $\mu\beta$ along the dipole moment direction is much larger for chromophore set **V**. Nevertheless, the increase in the SHG coefficient on proceeding from chromophore set **IV** to chromophore set **V** is unremarkable in most cases (~50% comparing chromophores **IVc** and **Vc**). The recent experimental study by Sen et al.[13] also reveals an increase in the response properties of tetraphenylporphyrin chromophores in which one of the β-positions is substituted by an $-NO_2$ group. However, this study aimed at reducing competitive charge transfer in the perpendicular direction, which is achieved by substituting all meso positions by donors and one β-position by an acceptor.

The effect of porphyrin bridge electron excessivity/deficiency is also illuminated by the results presented in Table 4. The hyperpolarizabilities of chromophores **Va** and **Vc** are larger than those of **Vd** and **Vf**. The smaller SHG coefficient of **Vb** compared to that of **Ve** is, however, surprising. The SHG coefficients of chromophore set **V** suggest that the effect of porphyrin skeletal electron excessivity or deficiency is only minimal, as there is very minimal variation in the response properties on switching the substitution pattern (**Va**–**c**

→ **Vd**−**f**). This is because the effective screening of the ground-state polarization by the excessivity of the porphyrin is reduced by the presence of the spacer groups. Note however that even though the effect of porphyrin electron excessivity and deficiency is negligible, having donor or acceptor substituents at the β instead of the meso position leads to larger EFISH coefficients since this substitution pattern leads to a single charge-transfer direction. Such a conclusion is substantiated by the recent experimental studies of Sen et al.[13]

Therefore, reducing the dihedral twist of the phenyl ring substituents with respect to the porphyrin plane and replacing the phenyl rings by electron-excessive and electron-deficient aromatic heterocycles leads to high-β porphyrin-based NLO chromophores. One efficient way to reduce the dihedral twist angle is by introducing intervening spacer groups between the porphyrin and the phenyl rings. Of the two spacer groups, azo and acetylenic, studied in this contribution, the azo linkage is more effective, since the azo group in addition to reducing the dihedral twist angle also leads to enhanced NLO response. The effect of the electron excessivity/deficiency of the porphyrin core itself on the NLO response properties appears to be minimal due to the presence of the intervening spacers and phenyl rings.

IV. Conclusion

By analyzing a variety of substitution patterns in porphyrinic chromophores, we have demonstrated that large second-order NLO responses in nonpolyene push−pull architectures can be obtained. Our earlier study on the effects of electron excessivity and deficiency of aromatic heterocycles on chromophore NLO response properties was employed here as a basis to design structures with nonresonant $\mu\beta$ values as high as 10 000 $\times 10^{-48}$ esu. The present results suggest that large NLO response properties in push−pull porphyrins can be achieved by as follows:

(1) Reducing the phenyl ring dihedral twist with respect to the porphyrin plane. One way to minimize these conjugation diminishing effects is by inserting intervening π-electron spacer groups such as alkenyl, azo, or alkynyl moieties between the phenyl groups and the porphyrin core. While all three spacers minimize the twist angle effects, the azo linkage is a much more effective bridge for enhancing NLO response.

(2) Modifying the electron excessivity or deficiency of the aromatic ring substituents appended to the porphyrin skeleton. On the basis of our earlier analysis, the most electron-excessive aromatic ring that can be appended to a donor substituent is pyrrole and the most electron-deficient aromatic ring that can be appended to an acceptor substituent is tetrazine. A combination of these substituents results in an almost 2-fold increase in NLO response compared to more conventional structures. Chromophores that combine points 1 and 2 lead to an almost 1 order of magnitude increase in NLO response over previously studied porphyrinic chromophores.

(3) Exploiting the electron excessivity and deficiency of the porphyrinic skeletal carbon atoms. While the enhancement in the NLO response achieved by this approach is not found to be universal in the chromophores discussed here, it should be possible to design new chromophores where even larger responses result. For example, one of the chromophores studied here (**Vc**) exhibits an enhancement of ∼150% in β.

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