First-Order Hyperpolarizabilities of Sulfophthalein Dyes

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In this paper we report the first hyperpolarizabilities (β) of 12 sulfophthalein dyes. Since these dyes are ionic in nature, their second-order nonlinearities were measured by the hyper-Rayleigh scattering technique in solution. The measured β values are large and highly solvent dependent. Inclusion of solvent polarity in ab initio estimates of static second-order polarizability does not fully account for the experimental β values. Contributions from the dissociated forms of the dye in different solvents seem to play an important role in enhancing β in these systems.

Introduction

Sulfophthalein dyes are widely used as acid—base indicators[1] as well as fluorescent probes in chemical and biological systems[2] to monitor transformations as a function of pH of the medium. The color of the dyes is yellow in weakly acidic solutions and turns to red when the pH is raised. The acid form is a singly charged ion, and the base form has two negative charges[3] (Figure 1). The color change is ascribed to the rehybridization of atoms from the unsymmetric resonance system to the symmetric form. All three forms, that is, the neutral, acidic, and basic forms, can be present, but a particular form may be dominant under certain conditions in a solvent.

The color change in these dyes can also be brought about by changing the polarity of the medium, since the more polar basic form is stabilized readily in a polar environment. In fact, Ramart et al.[4] observed large solvatochromic shifts in some sulfophthalein dyes on going from benzene (dielectric constant, D = 2.8) to water (D = 80) solvents. In other words, in a nonpolar solvent like chloroform the dyes exist mainly in their neutral form and exhibit their characteristic absorption. In a polar solvent like methanol, however, the dyes dissociate nearly completely, and the absorption is due to their acid form. In water the basic form of the dye contributes substantially, and in fact, the absorption maximum in some of the sulfophthalein dyes shifts to the red by ca. 150 nm on going from an acidic to an alkaline pH. The linear absorption properties of these dyes can, thus, be manipulated by changing the dielectric constant of the medium, and there is ample scope for determining their nonlinear optical properties in different solvents and using this knowledge to probe microenvironments inside a macromolecule. Also dye-doped polymeric systems[5,6] have shown tremendous potential for photonics application. Recently, Moylan[7] has investigated molecular hyperpolarizabilities of neutral amine-substituted coumarin dyes and predicted their suitability in electrooptic applications.

In this paper we have determined the first-order hyperpolarizabilities (β) of 12 sulfophthalein dyes using the recently developed hyper-Rayleigh scattering (HRS) technique.[8-13] This two-photon scattering technique is an ideal method for β measurements on ionic NLO chromophores,[14-16] such as the sulfophthalein dyes, in solution and particularly in polar solvents, which is not possible by the traditional electric field induced second-harmonic (EFISH) generation technique.[17] Semiclassical results on the static quadratic hyperpolarizability coefficient in the gas phase are contrasted with the experimental values. Solvent effects are dealt with at the ab initio level within the self-consistent reaction field (SCRF)[18] approach.

Experimental Section

Organic dyes **1–12** (Figure 1) were purchased from Aldrich, and all solvents were obtained commercially and purified using standard procedures. β values were measured in different solvents by the HRS technique. The experimental setup has been described in detail elsewhere.[13] In brief, the fundamental of a Q-switched Nd:YAG laser (Spectra Physics, 8 ns) is focused onto a glass cell containing the solute in solution. The second-harmonic scattered light is collected into a sensitive UV—visible photomultiplier tube. Other harmonics are eliminated by a set of filters. A small fraction of the 1064 nm fundamental is directed toward an IR sensitive photomultiplier tube (PMT) for monitoring the incident light intensity. Signals from both PMTs are fed into a gated boxcar averager (SRS 250) to record the intensities of the incident and second-order scattered light pulses after averaging over 1000 shots. All data are collected at laser powers ($\leq$12 mJ/pulse) well below the threshold for stimulated Raman and Brillouin scattering, self-focusing or self-defocusing, and dielectric breakdown.

The intensity of the HRS signal is given by (assuming that the values of β_{ijk} at two different points are correlated only over small distances compared to a wavelength)[19,20]

$$I_{2\omega} = GB^2 I_\omega^2 = G\sum_k N_k \beta_k^2 I_\omega^2 \qquad (1)$$

where G is an instrument factor and depends on the scattering geometry, N is the molecular number density, β is the first-order hyperpolarizability of individual molecules, and I_ω and $I_{2\omega}$ are, respectively, the incident and scattered intensities. For a two-component mixture of solvent and solute the scattering signal $I_{2\omega}$ is given by

$$I_{2\omega} = G\{N_{solvent}\beta_{solvent}^2 + N_{solute}\beta_{solute}^2\}I_\omega^2 \qquad (2)$$

The quadratic coefficient $I_{2\omega}/I_\omega^2$ is a linear function of the number density of the solute, N_{solute}, if β and N for the solvent are fixed. The intercept can be used to calculate the proportionality factor G, provided $\beta_{solvent}$ is known. The factor G depends on the wavelength, the distance between the cell and the detector, the solid angle of photon collection, and the PMT gain. This approach effectively eliminates the need for the knowledge of local field factors, since these factors are divided

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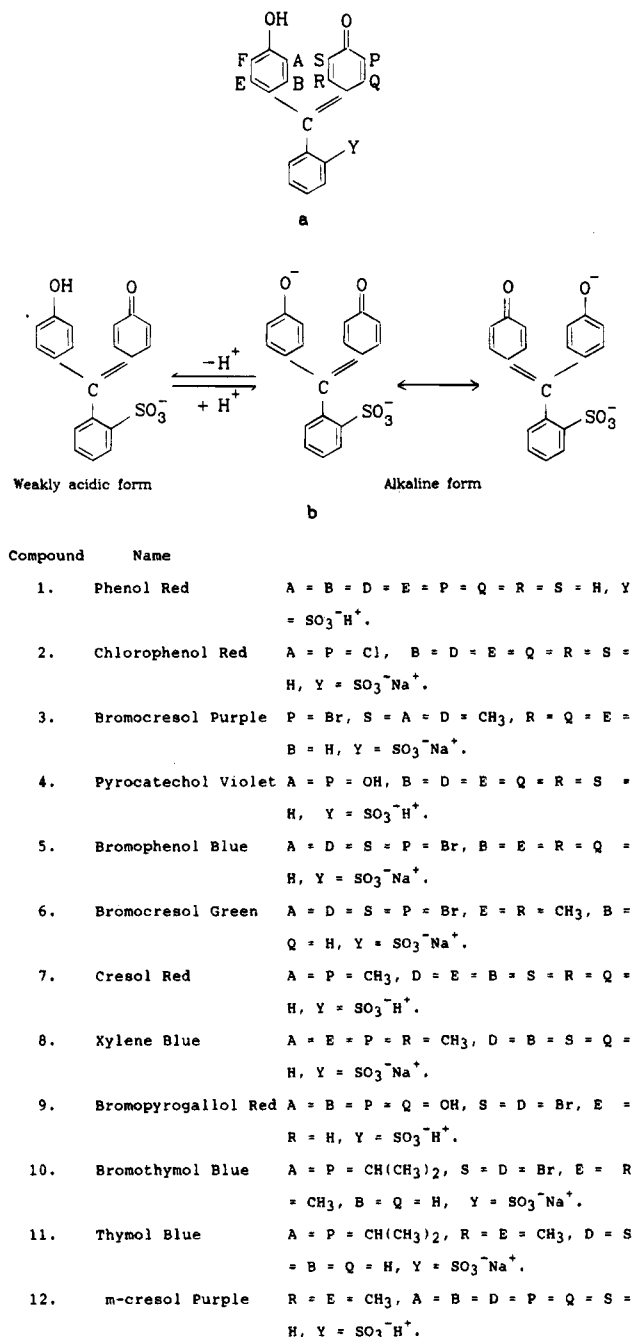**Figure 1.** (a) Structure of sulfophthalein dyes. (b) Structure change of sulfophthalein dyes with change of pH of the medium.

Compound	Name	
1.	Phenol Red	A = B = D = E = P = Q = R = S = H, Y = SO₃⁻H⁺.
2.	Chlorophenol Red	A = P = Cl, B = D = E = Q = R = S = H, Y = SO₃⁻Na⁺.
3.	Bromocresol Purple	P = Br, S = A = D = CH₃, R = Q = E = B = H, Y = SO₃⁻Na⁺.
4.	Pyrocatechol Violet	A = P = OH, B = D = E = Q = R = S = H, Y = SO₃⁻H⁺.
5.	Bromophenol Blue	A = D = S = P = Br, B = E = R = Q = H, Y = SO₃⁻Na⁺.
6.	Bromocresol Green	A = D = S = P = Br, E = R = CH₃, B = Q = H, Y = SO₃⁻Na⁺.
7.	Cresol Red	A = P = CH₃, D = E = B = S = R = Q = H, Y = SO₃⁻H⁺.
8.	Xylene Blue	A = E = P = R = CH₃, D = B = S = Q = H, Y = SO₃⁻Na⁺.
9.	Bromopyrogallol Red	A = B = P = Q = OH, S = D = Br, E = R = H, Y = SO₃⁻H⁺.
10.	Bromothymol Blue	A = P = CH(CH₃)₂, S = D = Br, E = R = CH₃, B = Q = H, Y = SO₃⁻Na⁺.
11.	Thymol Blue	A = P = CH(CH₃)₂, R = E = CH₃, D = S = B = Q = H, Y = SO₃⁻Na⁺.
12.	m-cresol Purple	R = E = CH₃, A = B = D = P = Q = S = H, Y = SO₃⁻H⁺.

out by measuring in nearly the same local field. The number densities of the solvent, $N_{solvent}$, and solute, N_{solute}, are calculated from the molecular weight and the density.

In the case of absorption of the light scattered at 2ω by the NLO molecules, a correction term has to be incorporated:[15]

$$I_{2\omega} = G\{N_{solute}\beta_{solute}^2 + N_{solvent}\beta_{solvent}^2\}I_\omega^2 \times 10^{-\epsilon(2\omega)Nl} \quad (3)$$

$\epsilon(2\omega)$ is the absorption cross section (in cm²) at the second-harmonic frequency, N is the number density (in cm⁻³) of the absorbing molecules, and l (in cm) is an effective optical path length. Since low concentrations (10^{-5}–10^{-8} M) of solute were used, we assume that the presence of the solute molecules does not change the number density of the solvent molecules, $N_{solvent}$, significantly. From the intercept and the slope of the plot of $I_{2\omega}/I_\omega^2$ vs number density, β_{solute} can be calculated provided $\beta_{solvent}$ is known. Maker et al.[20] calibrated carbon tetrachloride with respect to quartz, using the same HRS technique, and we

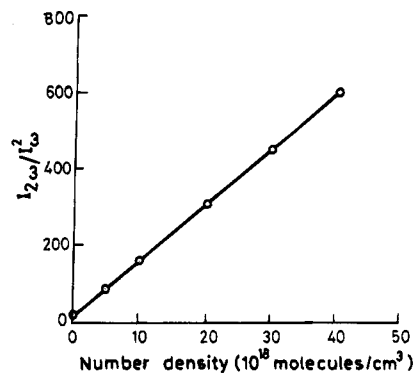**Figure 2.** Quadratic coefficient $I(2\omega)/I(\omega)^2$ (arb. units) vs the number density of compound **1** in acetone.
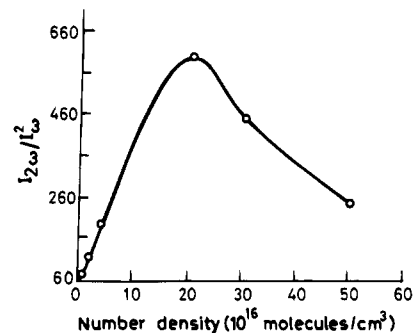

Figure 3. Quadratic coefficient $I(2\omega)/I(\omega)^2$ (arb. units) vs the number density of compound **6** in water.

have calibrated methanol, ethanol, ethylene glycol, acetone, water, and chloroform with respect to carbon tetrachloride by a method similar to that of Zyss et al.[18] We have obtained β_{water} = 0.05 × 10^{-30} esu, $\beta_{ethy.gly.}$ = 0.41 × 10^{-30} esu, $\beta_{methanol}$ = 0.52 × 10^{-30} esu, $\beta_{ethanol}$ = 0.61 × 10^{-30} esu, $\beta_{chloroform}$ = 0.48 × 10^{-30} esu, and $\beta_{acetone}$ = 0.42 × 10^{-30} esu. Figure 2 shows the $I_{2\omega}/I_\omega^2$ vs N_{solute} plot for compound **1** in acetone. From the intercept and slope we have calculated a value of $\beta_1^{acetone}$ = 101 × 10^{-30} esu. Figure 3 displays the same plot for compound **6** in water, where the dye molecule absorbs the harmonic scattered radiation at 532 nm significantly. No linear concentration dependene is observed in this case. We have used eq 3 to calculate the first-order hyperpolarizability of this compound and found β_6^{water} = 630 × 10^{-30} esu. Similarly, we have obtained β values for the other sulfophthalein dyes in water from eq 3 and in other solvents using eq 2.

UV–visible spectra of the compounds were recorded with freshly prepared solutions in different solvents in a Hitachi (U 3400) spectrometer at room temperature.

Results and Discussion

Table 1 lists measured β values for the 12 sulfophthalein dyes in six different solvents starting from the least polar chloroform to the most polar water. Generally, the dye molecules have significant second-order hyperpolarizabilities and the β value decreases as the dielectric constant or polarity of the solvent decreases. In water, however, we find some exceptions, and the reason for this will be discussed later in this part.

To estimate the gas phase β for comparison with the measured values, the geometry of each dye molecule was fully optimized using the PM3[21] parametrization available in the MOPAC[22] package. This method is extremely reliable for obtaining the ground state geometry of organic molecules. The SO₃Na functional group in several dyes was first replaced with a SO₃H group since the optimized parameters for Na are not available in MOPAC. But this small alteration is unlikely to change the

TABLE 1: Second-Order Polarizability Measured by the HRS Technique, $\beta_{solvent}$ ($\times 10^{30}$ esu), in Six Different Solvents[a]

compd	β_{water}	$\beta_{ethy.\ gly.}$	$\beta_{methanol}$	$\beta_{ethanol}$	$\beta_{acetone}$	$\beta_{chloroform}$
1	610(110)	180(99)	170(91)	164(84)	101(76)	53(40)
2	540(128)	230(112)	186(104)	171(91)	129(80)	70(48)
3	610(135)	238(118)	193(110)	176(94)	136(82)	80(55)
4	559(139)	244(126)	200(118)	180(100)	141(90)	86(60)
5	620(148)	253(136)	212(128)	193(116)	156(103)	94(70)
6	630(162)	257(140)	215(130)	197(120)	160(105)	97(74)
7	529(170)	264(147)	220(134)	200(125)	166(110)	99(78)
8	602(178)	271(155)	230(140)	208(130)	171(113)	101(80)
9	560(185)	280(157)	236(144)	211(138)	175(127)	110(86)
10	628(188)	291(160)	240(150)	216(137)	180(121)	114(90)
11	580(190)	308(172)	254(168)	227(146)	192(133)	124(99)
12	640(200)	320(180)	260(174)	233(151)	198(140)	130(104)

[a] Ab initio static hyperpolarizability, β_{calc} ($\times 10^{30}$ esu), are given in parentheses next to the measured values.

TABLE 2: Calculated Dipole Moment, μ_g (in D), Semiempirical Gas Phase Static Hyperpolarizability, β_g ($\times 10^{30}$ esu), and Quadratic Hyperpolarizability Measured by the HRS Technique $\beta_{chloroform}$ ($\times 10^{30}$ esu), of 1–12

compd	μ_g	β_g	$\beta_{chloroform}$
1	5.24	30.9	53
2	5.29	34.3	70
3	5.47	37.6	80
4	5.6	38.7	86
5	5.18	40.2	94
6	5.09	41.6	97
7	5.43	55.4	99
8	5.48	57.5	101
9	5.83	58.6	110
10	6.1	63.4	114
11	5.11	68.2	124
12	5.33	79.2	130

optimized structure much. Molecular first-order hyperpolarizabilities were then computed using the finite field method.[23] The calculated β values are gas phase numbers and are listed in Table 2 along with the ground state dipole moments which are readily obtained from the calculation. These static β values are contrasted with the measured quantities in the least polar solvent used in this study, that is, chloroform. Although the trend is reproduced in the calculations nicely, the β values in chloroform ($D = 4.8$) are ca. 1.5-fold higher than the gas phase ($D = 1$) hyperpolarizabilities. In fact, it has been pointed out earlier that the solvent polarity exerts an important influence on the second-order NLO response in molecules.[14] From Table 1, it is clear that all the compounds exhibit very high second-order nonlinearity and β increases as a function of dielectric constant of the solvent. To explicitly take into account the solvent polarity effects, we have adopted Onsager's self-consistent reaction field (SCRF) approach as implemented in the GAUSSIAN-92[24] set of programs. We have obtained the static β values at the Hartree–Fock ab initio level using a split valence (3-21G*) basis set. Such a theoretical treatment has been reported recently to yield excellent trends in comparison to experimental hyperpolarizabilities in conjugated systems.[14] In its simplest form, the solute is considered to be occupying a spherical cavity of radius a_0 in a solvent continuum of dielectric constant D. The permanent dipole moment of the solute will induce a reflection dipole in the solvent molecules surrounding it. This electrostatic interaction, which leads to solvation, is treated as a perturbation to the Hartree–Fock Hamiltonian, which relates the molecular dipole operator (μ) with the reaction field, R, in the following manner:

$$R = k\mu \tag{4}$$

where the proportionality constant k gives the strength of the

reaction field. This constant is related to the dielectric constant of the medium D in a straightforward way.

$$k = 2(D - 1)/\{(2D + 1)a_0^3\} \tag{5}$$

The calculation continues until self-consistency is achieved in the presence of the reaction field.

In our method, the PM3 optimized structures were used for molecular first-order hyperpolarizability calculations except for two modifications: (1) The O–Na bond length obtained from the optimized ab initio geometry of p-hydroxybenzoic acid using a split-valence (6-31G*) basis set was used for SO_3Na-containing compounds, and (2) Br atom was replaced by Cl atom whenever applicable, but otherwise the rest of the geometry was kept unchanged from the PM3 optimized structure. The ab initio β values are listed along with the experimentally measured values in Table 1. The calculated numbers are much higher than the gas phase values but still lower than the measured quantities. For example, m-cresol purple (compound **12**) has a semiempirical gas phase $\beta = 79.2 \times 10^{-30}$ esu, whereas its ab initio $\beta = 104 \times 10^{-30}$ esu in chloroform after taking into account the solvent polarity. But the measured value in chloroform ($\beta = 130 \times 10^{-30}$ esu) is still higher by a factor of 1.3. The disagreement is worse as we move to higher dielectric constant solvents.

The difference between the measured and calculated hyperpolarizability may be accounted for in several ways. We have observed earlier[15] that β of a weak organic acid which dissociates partially in solution is a sum of the contributions from the dissociated and undissociated forms weighted appropriately by the degree of dissociation. First-order hyperpolarizabilities of the different (neutral or charged) forms are different. In sulfophthalein dyes, which remain predominantly in the acidic form in most of the solvents employed in this work, β will strongly depend on the amount of the dissociated form present. In polar solvents like water, the degree of dissociation is large, and the measured β reflects mainly the first hyperpolarizability of the anionic forms of the dye. The ab initio values reflect the first hyperpolarizability of the dyes strictly in their neutral, that is, undissociated, form. Therefore, in chloroform and acetone, in which the dissociation does not progress well, we find a closer agreement between the theoretical and experimental numbers. It is noteworthy that although a particular form (neutral, acidic, or basic) of a dye is predominant in a solvent, the other forms are also present in small amounts, as shown by the equilibrium in Figure 1.

A lower value of β is not surprising since of all solvent parameters that affect β, only the solvent dielectric constant is accounted for in our calculation. If we plot a reduced solvent parameter containing the dielectric constant of the solvent, that is, $(D - 1)/(2D + 1)$ vs β for the dyes studied here, we find the behavior shown in Figure 4. This is far from the linear behavior observed for p-nitroaniline in different solvents.[25] Intermolecular hydrogen bonding between the dye and the solvent molecules cannot be ruled out. In particular, this will be very important in water, ethylene glycol, methanol, and ethanol solvents. Effects related to electron correlation and frequency dispersion are also not explicitly considered in our simplistic calculations. Both types of effects increase the value of β. In Table 3 the wavelengths of maximum absorption of all 12 dyes in six different solvents are listed. Figure 5 shows the dependence of β on λ_{max} in different solvents. It is apparent that as the solvent polarity changes, the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO) varies. β is highest in water, in which the wavelength of maximum absorption is also the longest. In fact, in water all the dyes absorb strongly at 532 nm and resonance
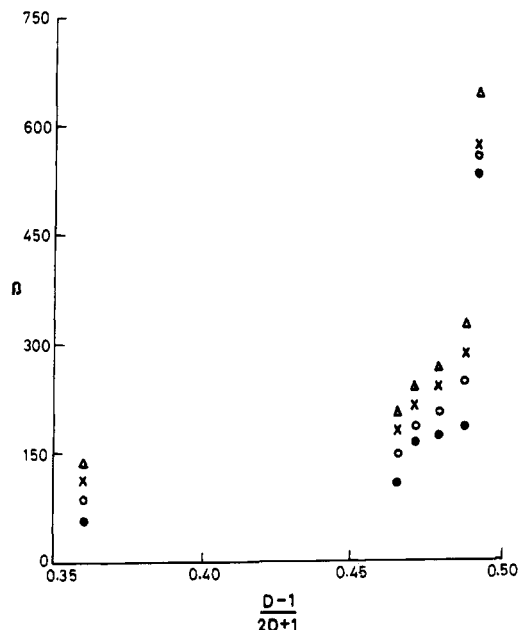
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Figure 4. Plot of β ($\times$ 10^{30} esu) vs $D - 1/2D + 1$, for compounds **12** ($\triangle$), **9** ($\times$), **4** ($\bigcirc$), and **1** ($\bullet$) in different solvents.

TABLE 3: λ_{max} **of Different Dyes in Different Solvents**

compd	water	ethy. gly.	methanol	ethanol	acetone	chloroform
1	556	448	432	424	412	396
2	575	452	433	428	416	388
3	585	444	430	422	413	390
4	570	432	422	412	406	385
5	589	449	435	424	414	387
6	612	470	455	438	421	392
7	579	446	428	423	417	393
8	586	449	430	420	411	395
9	552	442	430	422	414	389
10	615	478	448	437	415	402
11	615	468	449	438	418	395
12	580	443	420	413	408	388
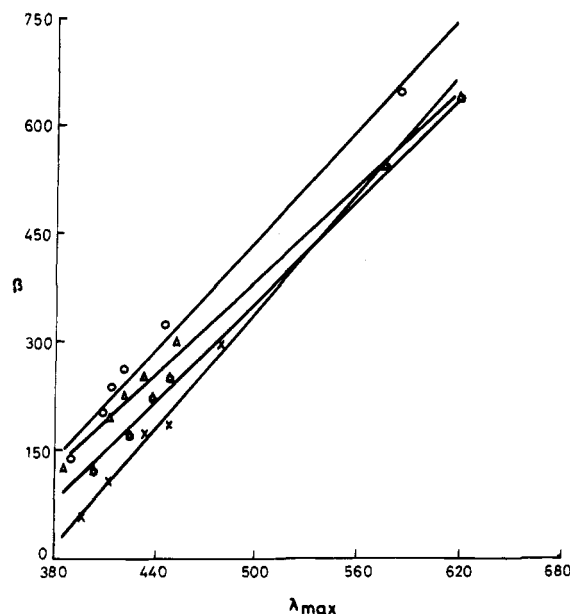
Figure 5. Plot of β ($\times$ 10^{30} esu) vs λ_{max}, for compounds **12** ($\bigcirc$), **9** ($\triangle$), **4** ($\bullet$), and **1** ($\times$) in six different solvents.

enhancement is, perhaps, responsible for large β values. In addition, it is believed that these sulfophthalein dyes exist mainly in three colored species in aqueous solution, one of which is the quinonoid alkaline form.[26] This implies that the first-order hyperpolarizability of these dyes in pure water actually originates from three different contributions: the neutral, weakly acidic,

and alkaline forms. Although the alkaline form dominates, the other forms are present in small amounts. The relative occurrence of a particular form varies from one dye to the other, and as a result, we observe no regular trend in the measured hyperpolarizabilities in water.

Conclusion

We have critically examined the first-order hyperpolarizabilities of 12 sulfophthalein dyes in solvents of varying polarity. The large first-order hyperpolarizabilities of these molecules can be further improved by reducing the low-energy excitation gap with an appropriate choice of a solvent or by choosing an appropriate microenvironment where the singly ionized weakly acidic form and/or the doubly ionized weakly alkaline form of the dye is stabilized. Because of their easy availability and large second-order nonlinear coefficients, these dyes may find application as nonlinear optical probes in the interior of a polymeric or biological molecule. The dynamic range for second-order polarizability of these dyes as a function of solvent polarity is much larger than their linear absorption properties. Also, designing a suitable polymer system where these chromophores can be stabilized in a polar environment in the matrix holds promise for new electrooptic materials.

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