6636 J. Am. Chem. Soc. 1994, 116, 6636–6640

Chromophore Structure, Second Harmonic Generation, and Orientational Order in Zirconium Phosphonate/Phosphate Self-Assembled Multilayers

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Received March 17, 1994[⊗]

Abstract: Two new phosphonate-terminated polar azo dyes, one that is substantially rigid (**1**) and the other with a large molecular hyperpolarizability (**2**), were designed and incorporated into zirconium-based surface multilayers. Second harmonic generation (SHG) was observed from the multilayers as a function of incident and polarization angles and compared with that from the previously reported aminophenylazophenylphosphonic acid chromophore **3**. The new dyes are analogous to moieties commonly used in electric field-poled polymers, allowing comparisons between the polymers and the multilayers. Apparent order parameters $\langle\cos^3\theta\rangle$ are >0.2 for **1** and ~0.16 for **2**. Because of local field effects, the value for **1** is probably a lower limit. Use of other dyes that are both rigid and highly polar led to H-aggregation. Insertion of a nonpolar chromophore layer among the polar layers had no effect on SHG. The syntheses involved several novel reactions, involving the preparation of an unsymmetrically substituted diphenylpiperazine, an anilinoalkyl phosphonate, and the deprotected phosphonic acids themselves.

Introduction

Organic materials with large second order nonlinearities are currently under development for applications in second harmonic generation (SHG), electrooptics, and for use as photorefractives.[1] Generally these systems consist of molecular subunits with large hyperpolarizabilities organized in noncentrosymmetric (usually polar) bulk arrangements. A large fraction of recent work has focused on the stability of the induced orientational order[2] in these materials, especially structural relaxation of electric field-poled polymers. This work is important because the maintenance of order at high temperatures is essential for many device applications. This issue of structural stability is also of concern for other classes of materials such as molecular crystals and Langmuir–Blodgett films.[3] An important new area of interest has been the incorporation of additional molecular functionality to enable photocharge generation and otherwise modify bulk material behavior.[4]

We recently described a strategy[5] for producing thermally stable second order nonlinear optical films,[6] taking advantage of zirconium phosphonate/phosphate coordinative bonding[7] to fix layers of a polar azo dye to each other, utilizing a three-step, polar deposition sequence of surface phosphorylation, zirconation, and dye adsorption. The resulting structure is shown schematically in Figure 1. These films[6] showed relatively large second harmonic coefficients comparable in magnitude to that of $LiNbO_3$; in addition, the films were stable to orientational randomization up to 150 °C. Important here is that the general strategy of this deposition chemistry is amenable to the incorporation of other functional units at predetermined spacings and relative orientations. The chromophore studied in the original work was selected primarily for ease of synthesis and handling but did not possess a well-understood electron accepting substituent and gave unexpectedly large bulk values of d_{zxx} and d_{xxz} when assembled. As such, it was not possible to derive an unambiguous polar order parameter from the data.

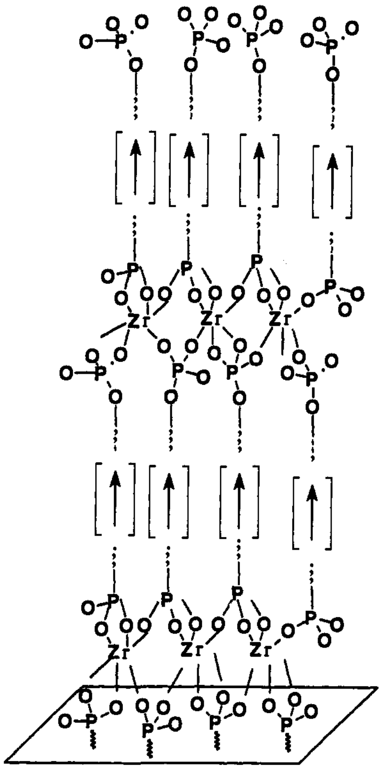

Figure 1. Idealized schematic diagram of a polar Zr–P multilayer. The bracketed arrows represent polar chromophores.

In this paper, we report the synthesis and polar film formation of two new nonlinear chromophores, **1** and **2**. The first, which

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1994.

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Table 1. NMR Spectra of Piperazine Derivatives

compound (solvent)	ArH	piperazinyl-H	other
4(CDCl,	6.85(d), 6.90(t), 6.97(d), 7.32(t), 7.38(d)	3.4	
5($CDCl_3$)	6.90(d of d), 6.98(d), 7.31(d of d), 7.73(d of d)	3.34, 3.48	1.30(t), 4.15(m)
6($CDCl_3$)	6.98(m), 7.05(d), 7.74(d of d), 7.95(d), 8.05(abq)	3.52, 3.63	1.31(t), 3.41(t), 4.1(t and m)
1(DMSO-d_6)	7.03(d of d), 7.19(d), 7.56(d of d), 7.92(d), 8.00(d), 8.04(d)	3.48, 3.59	3.51(t), 3.72(t)
11(DMSO-d_6)	7.00(d of d), 7.15(d), 7.52(d of d), 7.89(d0, 8.00(d), 8.40(d)	3.40, 3.63	
12(DMSO-d_6)	7.03(d of d), 7.16(d), 7.52(d of d), 7.87(d), 7.95(d), 8.23(d)	3.45, 3.62	3.68(t), 4.30(t), 8.48(s)

Table 2. NMR Spectra of Propylphosphonate Derivatives

compound (solvent)	ArH	propyl-H	other
7($CDCl_3$)		1.8(m), 2.1(m), 3.22(t)	1.29(d of d), 4.65(m)
8($CDCl_3$)	6.67(m), 7.22(m)	1.7(m), 1.85(m), 3.36(t)	1.31(d of d), 2.91(s), 4.65(m)
9($CDCl_3$)	6.75(d), 7.89(d), 7.99(abq)	1.75(m), 1.95(m), 3.54(t)	1.30(d of d), 3.08(s), 4.70(m), 10.02(s)
10(DMSO-d_6)	6.89(d), 7.86(d), 7.91(d), 8.03(d)	1.55(m), 1.70(m), 3.55(t)	3.09(s), 10.02(s)
2(DMSO-d_6)	6.91(d), 7.80(d), 7.92(d), 8.22(d)	1.57(m), 1.77(m), 3.55(t)	3.10(s), 8.48(s)

has a sulfone acceptor, was designed for maximum rigidity within the guidelines imposed by the deposition process, while the second, which has a cyanovinyl acceptor, was chosen because of its high anticipated molecular hyperpolarizability β.[8] The sulfone chromophore of **1** is also of interest[9] because of its relative transparency in the visible region of the spectrum and its high thermal stability. Both species are advantageous over the original azo dye, **3**, in that the donor–acceptor substituent pairs are analogous to those used in other molecules with measured values of β that have been incorporated in materials whose SHG coefficients and order parameters were measured. Thus, it is possible to relate directly SHG data from layers of **1** and **2** to published SHG results on analogous molecules with known degrees of polar order to estimate order parameters for our own materials. Furthermore, **3** is somewhat basic, and the bulk nonlinearity of layers of **3** may include contributions from its protonated form. Because **1** and **2** contain stronger electron withdrawing substituents, they should be less susceptible to protonation, and their nonlinear optical activity should be directly attributable to β of the neutral molecules.

Experimental Section

General. NMR spectra were obtained on a Bruker 360 MHz instrument. UV–vis spectra were recorded on a Hewlett-Packard diode array spectrometer. Elemental analyses were performed by Robertson Microlit Laboratories, Madison, NJ. Layers were deposited on clean glass slides, Si wafers, and quartz disks from solutions of **1**, saturated in 20% *N,N*-dimethylacetamide–80% EtOH, and **2**, 35 mg/50 mL in EtOH, by dipping zirconated phosphate or phosphonate-rich surfaces in the nearly boiling solutions as previously described.[6] Acidity of pH 2–3 was maintained by adding 4 N HCl in dioxane to the dye solutions. Rephosphorylation and rezirconation were accomplished using $POCl_3$ and collidine in CH_3CN and $ZrOCl_2$ in H_2O, respectively. Ellipsometry was carried out as reported earlier.[5]

1-(4-Bromophenyl)-4-phenylpiperazine (4). A mixture of 15.7 g of 4-bromoaniline (0.091 mol), 20.0 g of *N,N*-bis(2-chloroethyl)aniline (0.092 mol), 16 g of $NaHCO_3$, 2 g of NaI, and 20 g of ethylene glycol was heated slowly to 110 °C. A vigorous reaction occurred above 100 °C. After 1 h at 110 °C, the mixture was allowed to cool and triturated with 2 × 100 mL of H_2O. The residue was dissolved in a mixture of 100 mL of C_6H_6 and 50 mL of EtOH, filtered hot, diluted with 150 mL of EtOH, concentrated by boiling to 250 mL, and allowed to crystallize. The yield was 16.8 g of light beige solid (58%), mp 160–164 °C, pure by NMR (see Table 1).

Diethyl 4-(4-Phenylpiperazinyl)phenylphosphonate (5). A portion of the above solid (6.0 g, 0.020 mol) was stirred in 140 mL of distilled tetrahydrofuran at –78 °C under N_2. An equivalent amount of *n*-BuLi in hexane was added. The solids dissolved and then reprecipitated. After 10 min, diethylchlorophosphate (3.6 g, 0.021 mol) was added. After 1 h at –78 °C, Et_2O and aqueous $NaHCO_3$ were added, forming two layers. After reaching room temperature, the organic layer was concentrated to 7.9 g of crude solid that was 85% pure. Chromatography on 75 g of silica gel, eluting with CH_2Cl–EtOAc mixtures, gave 5.1 g (72%) of white, crystalline solid, pure by NMR (see Table 1).

In addition, the routine Me_3SiBr dealkylation of **5** followed by coupling with *p*-nitrophenyldiazonium BF_4 in AcOH gave **11**, which was recrystallized from DMSO–EtOH with difficulty. Formylphenylazo coupling, dealkylation, and Knoevenagel condensation of **5** (as described for **2**) gave **12**. While pure by NMR, these compounds could not be freed from inorganic impurities.

Diethyl (4-(4-(4-(4-((2-Hydroxyethyl)sulfonyl)phenyl)azo)phenyl)-piperazinyl)phenyl)phosphonate (6). 4-(2-Hydroxyethyl)sulfonylaniline hydrochloride was prepared by the reduction,[10] hydroxyethylation,[11] and hydrolysis[11] of 4-acetamidobenzenesulfonyl chloride. The aniline salt (0.91 g, 3.8 mmol) was diazotized in 3.5 mL of 2 N HCl with 230 mg (3.3 mmol) of $NaNO_2$ dissolved in 2 mL of H_2O and added dropwise at 5 °C. After 15 min at this temperature, the mixture was added to 1.05 g (2.8 mol) of **5** dissolved in 5 mL of propanoic acid at 5 °C. A red solution resulted. While keeping the temperature below 10 °C, NaOAc was added until the pH was 4, followed by 2 mL of H_2O. After stirring 4 h with ice bath cooling, the mixture was allowed to warm to room temperature overnight. A fine orange-red powder was collected and washed with 50% aqueous EtOH: yield 1.44 g (88%), pure by TLC and NMR (see Table 1).

(4-(4-(4-(4-(2-Hydroxyethyl)sulfonyl)phenyl)azo)phenyl)piperazinyl)-phenyl)phosphonic Acid (1). A solution of 420 mg of **6** in 50 mL in anhydrous CH_2Cl_2 was treated with 2.1 g of Me_3SiBr and 15 drops of pyridine for 24 h. The silanes were hydrolyzed with 1 mL of H_2O, and solvents were decanted from a red gum. Solids were obtained from the gum by precipitation with EtOH–H_2O: yield 0.36 g (95%). Recrystallization was from dimethylformamide–EtOH–Et_2O. The yield of purified product was 66 mg (48%): NMR (see Table 1); UV–vis max (EtOH) 426 nm. Anal. Calcd for $C_{24}H_{27}N_4PSO_6$: C, 54.33; H, 5.13; N, 10.56; P, 5.84; S, 6.04. Found: C, 54.61; H, 5.65; N, 10.40; P, 5.52; S, 5.92.

Bis(1-methylethyl) (3-Iodopropyl)phosphonate (7). A mixture of 75 g of 1,3-diiodopropane and 105 g of triisopropylphosphite was heated at reflux for 2 h. The mixture was allowed to cool and concentrated by rotary evaporation to 95 g. Chromatography on four times the weight of silica gel, eluting with hexane–EtOAc, gave a fraction that contained equimolar amounts of **7** and triisopropylphosphite. Concentration at 60 °C under vacuum gave **7** suitable for further transformation: NMR (see Table 2).

Bis(1-methylethyl) (3-(*N*-Methyl-*N*-phenylamino)propyl)phosphonate (8). A mixture of 15 mmol each of **7** and *N*-methylaniline, prepared with ice cooling, was stirred as a mixture of 3 g of $NaHCO_3$ and 20 mL of H_2O were added slowly. The mixture was heated at reflux overnight. One hundred milliliters each of Et_2O and H_2O was added. The Et_2O

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(8) The *p*-dimethylamino β-cyanocinnamate ester unit has a hyperpolarizability close to that of *N,N*-dimethyl-*p*-nitroaniline (Sohn, J. E.; Singer, K. D., unpublished results). Thus, the α-cyanovinylcarboxylate group is similar to nitro as an acceptor in NLO chromophores.

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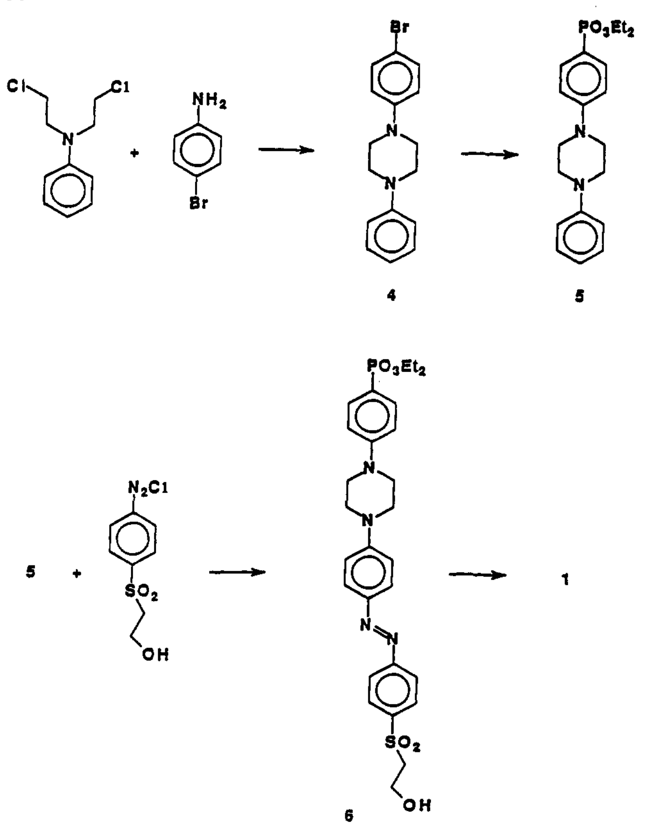
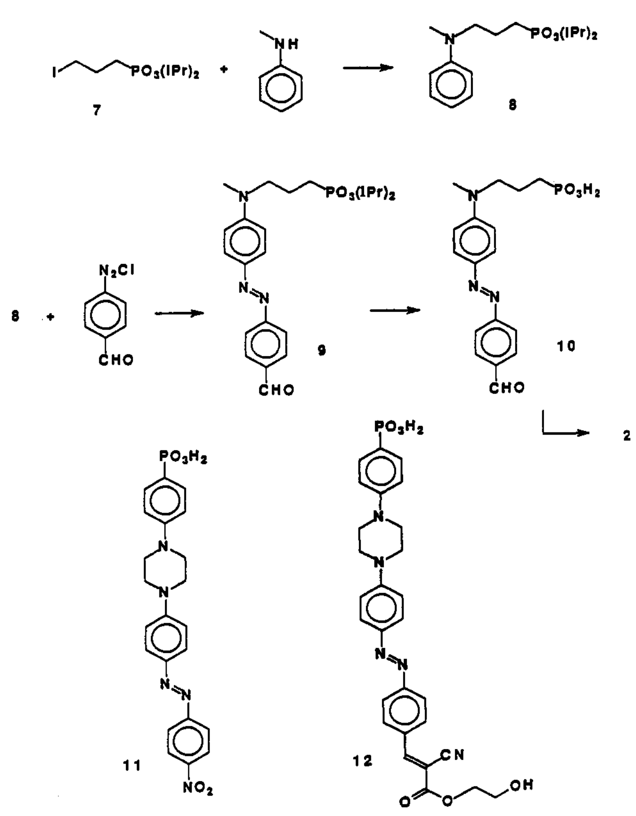
Scheme 1



Scheme 2



layer was extracted with dilute HCl, the extract was neutralized with Na_2CO_3, and the resulting mixture was extracted with Et_2O. This latter organic extract was dried with Na_2SO_4, filtered, and concentrated to 4.4 g of 90% pure product: NMR (see Table 2).

Bis(1-methylethyl) (3-*N*-Methyl((4-((4-formylphenyl)azo)phenyl)amino)propyl)phosphonate (9). Predominantly monomeric 4-aminobenzaldehyde (2.4 g, 20 mmol) was stirred in 10 mL of H_2O and 2 mL of concentrated HCl at 5 °C. This temperature was maintained as 1.24 g of $NaNO_2$ (18 mmol) dissolved in 3 mL of H_2O was added dropwise. The resulting mixture was stirred for 15 min, after which **8** (4.2 g, 13 mmol) and NaOAc (3.5 g) were added, still keeping the temperature ≤ 5 °C. Stirring was continued 6 h with ice bath cooling followed by 15 h at ambient temperature. Supernatant liquid was decanted from a red oil and extracted with 25 mL of CH_2Cl_2. The oil was dissolved in 100 mL of CH_2Cl_2, and the combined organics were washed with 100 mL of H_2O, dilute HCl, and concentrated $NaHCO_3$, dried, filtered, and concentrated to 6.5 g. Chromatography on 30 g of silica gel, eluting with CH_2Cl_2, CH_2Cl_2 + EtOAc, and EtOAc, gave 3.1 g (52%) of **9**: NMR (see Table 2).

3-(*N*-Methyl-((4-((4-formylphenyl)azo)phenyl)amino)propyl)phosphonic Acid (10). Ester **9** (10.6 g) was dissolved in 5 mL of CH_2Cl_2, and 1 g of Me_3SiBr was added. After stirring for 16 h, the volatiles were removed, and a solution of 0.25 mL each of pyridine and H_2O in 5 mL of EtOH was added. Concentration gave 0.86 g of solids, including 1.5 equiv of pyridine: NMR (see Table 2).

(3-((4-((4-(2-Cyano-2-((2-hydroxethoxy)carbonyl)ethenyl)phenyl)azo)phenyl)-*N*-methylamino)propyl)phosphonic Acid (2). A sample of **10** (0.65 mmol) was heated in 5 mL of EtOH and 0.1 mL of pyridine with 0.8 mmol of 2-hydroxyethyl cyanoacetate (prepared from ethylene glycol and cyanoacetic acid by heating in the presence of toluenesulfonic acid) just below boiling. After 6 h, the mixture was allowed to cool. The solids that settled were isolated and triturated with EtOH, Et_2O, deionized H_2O, dilute aqueous AcOH, EtOH, and Et_2O: yield 210 mg (68%) of dark red solid; NMR (see Table 2); UV–vis max (EtOH) 495 nm. Anal. Calcd for $C_{22}H_{25}N_4PO_6$ + $0.5H_2O$: C, 54.89; H, 5.65; N, 11.62; P, 6.44. Found: C, 55.0; H, 5.3; N, 11.4; P, 6.3.

Results and Discussion

Syntheses. Compounds **1** and **2** were prepared as shown in Schemes 1 and 2, respectively. We have already employed **7** in a viologen synthesis[12] and find it a convenient phosphonylalkylating reagent. The iodide is cleanly substituted without elimination or loss of esters. The Me_3SiBr dealkylations of **6** and **9** require large excesses of reagents but are highly selective considering the degree of functionalization.

The synthesis of **4** was carried out using new, improved conditions for the piperazine cyclization,[13] which may be useful in the synthesis of liquid crystalline rigid rod molecules.[14] Here, the piperazine ring substantially isolates the PO_3H_2 surface-active group from the nonlinear optical chromophore, while providing a nearly linear linkage between the two.

Depositions. The quantities of **1** and **2** deposited in each cycle of substrate immersion in $POCl_3$, $ZrOCl_2$, and dye solutions, as judged from absorbance and ellipsometry, were similar to what has been found previously (and reproduced during this work) for **3**. The absorbance at λ_{max} per layer (on both sides of a glass slide) was 0.23, and the ellipsometric thickness per layer (on one side of a Si wafer) was ~25 Å, in keeping with the azo dye character of all three compounds and the longer molecular lengths of **1** and **2**. However, the observation of aggregation and severe tilting in these layers (vide infra) calls both of these measures into question.

Second Harmonic Generation. All second harmonic data were obtained using the apparatus described in detail in reference 6. The fundamental wavelength was 1.064 μm, with the second harmonic near resonant with the chromophore molecular electronic transition. Because of the similarities in the electronic origins of SHG for the polar molecules used, we assume equivalent mechanisms of resonant enhancement of $\chi^{(2)}$. In general, the susceptibility (neglecting damping) is written as[15]

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Table 3. SHG Coefficients and Order Parameters for Selected NLO Materials

material	ref	d(1.06 μm) (10^{-9} esu)	N (10^{20} cm^{-3})	β(1.06 μm) (10^{-30} esu)	P	$P(1)^b$	$P(2)^c$
poled stilbene dye	18	2	0.9	430	0.04^a	0.31	0.25
poled sulfone dye	19	100	7	150	0.34	0.14	0.12
poled DR1	20	36	2.7	1060	0.07^a	0.22	0.18
sulfonylaniline LB film	21	12	7	13	0.4	0.12	0.10
azosulfone LB film	22	150	7	150	0.74	0.21	0.17
multilayer of **1**	this work	48	8	150	0.20^d		
multilayer of **2**	this work	280	8	1060	0.16^d		

[a] Calculated from the μE product. [b] P for a multilayer of **1** calculated from eq 2 using input from this row. [c] P for a multilayer of **2** calculated from eq 2 using input from this row. [d] Average values from columns P(**1**) and P(**2**).

$$\chi^{(2)}(\omega;\omega_1,\omega_2) = \left[\frac{N}{\epsilon_0}\frac{1}{2!}\right]\sum_{\alpha,\beta,\gamma}\rho^{e}_{\alpha\alpha}\left[\frac{d_{\alpha\beta i}d_{\beta\gamma j}d_{\gamma\alpha k}}{(\omega_{\alpha\gamma}-\omega_2)(\omega_{\alpha\beta}-\omega_1-\omega_2)} + \frac{d_{\alpha\beta j}d_{\beta\gamma i}d_{\gamma\alpha k}}{(\omega_{\alpha\beta}+\omega_1)(\omega_{\alpha\gamma}-\omega_2)} + \frac{d_{\alpha\beta j}d_{\beta\gamma k}d_{\gamma\alpha i}}{(\omega_{\alpha\beta}+\omega_1)(\omega_{\alpha\gamma}+\omega_1+\omega_2)}\right] \quad (1)$$

Here the α's and β's are the electronic states of the system, ω, ω_1, and ω_2 are the output and two input wavelengths. For SHG $\omega_1 = \omega_2$ and $\omega = 2\omega$. The first term in the bracket gives rise to the enhancement expected when α and β are the ground and first excited state respectively. The polarization and angle of incidence dependences of the SHG signal allows us to access the relative ratios of the tensor elements for a particular multilayer material. It was shown by Dick et al.[16] that the intensities of p- and s-polarized SHG respectively are

$$I^{2\omega}_{p}(\theta) = I^{2\omega}_{pp\rightarrow p}\cos^4\theta + I^{2\omega}_{ss\rightarrow p}\sin^4\theta + [I^{2\omega}_{pp\rightarrow p}I^{2\omega}_{ss\rightarrow p}]^{1/2}\cos\phi\,\sin^2(2\theta) \quad (2a)$$

$$I^{2\omega}_{s}(\theta) = I^{2\omega}_{sp\rightarrow s}\sin^2(2\theta) \quad (2b)$$

Here the $I^{2\omega}$'s are directly related to the magnitude of the tensor components of $\chi^{(2)}$, (and therefore the d coefficients), scaled by the angle of incidence and the revelant Fresnel factors. In eq 2, ϕ and θ, are the phase and polarization angles, respectively. Clearly with a limited number of measurements one can gain insight into the molecular polarizability of the chromophore studied.

SHG coefficients for multilayers of **1** and **2** are listed in Table 3. We also reproduced the four-layer intensity previously reported for **3**. For **1**, values were obtained after phosphorylation and zirconation of the last layer, which led to enhanced intensities while not affecting the UV–vis spectrum. This cross-link-induced orientation has been previously postulated.[17] The intensities were proportional to the square of the number of layers (6 vs 4 layers of **1**, 6 and 10 vs 4 layers of **2**), as expected for layers with reproducible polarity. The insertion of a layer of p-bis(4-phosphonostyryl)benzene[23] between layers 2 and 3 of four-layer samples of **1** and **3** had no significant effect on the intensity, pointing out the possibility of integrating electron donors and acceptors within the nonlinear optical material. SHG of **1** and **3** on quartz disks was half that obtained on microscope slides.

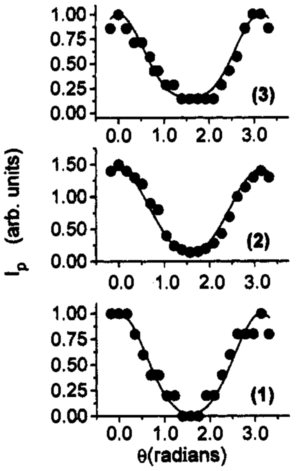
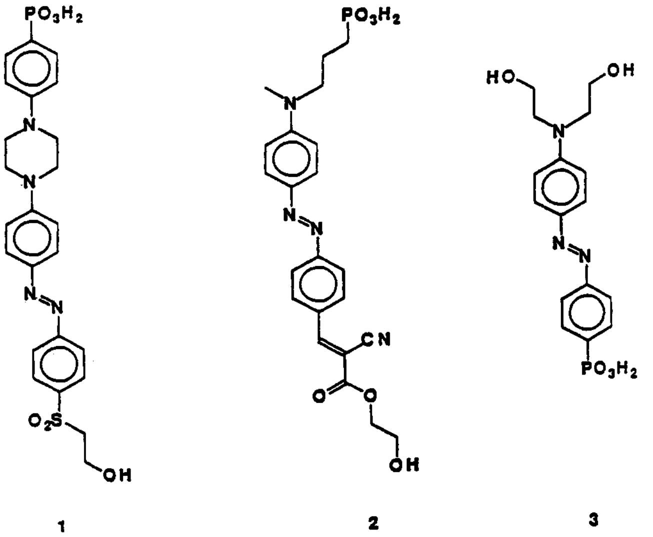


Figure 2. Relative p-polarized SHG as a function of input polarization for **1**, **2**, and **3**. Input polarization angle of zero corresponds to all-p input. Dots are experimental data, and curves are fits to eq 2. (The heights of the curves are not indicative of the absolute efficiencies of the three materials.)

Chart 1



The polarization dependences of SHG from 4-layer samples of **1**, **2**, and **3** are compared in Figure 2. The solid lines through the data are fits to eq 2. In contrast to what has been observed for **3**, the $S_{in}P_{out}$ signal for **1** is approximately zero (within our signal to noise), consistent with SHG arising predominately from β_{zzz} of the molecules and indicating a negligible value of d_{zxx} in the material. This is as expected for a polar film with azimuthal symmetry. We are thus able to make the simplifying assumption[24] that virtually all the SHG contributes to d_{zzz}, which was not the

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case for **3**. Since the SHG for **1** is half that observed for **3**, $|d_{zzz} \sin^2 \theta_f| = 6$ pm/V, $\theta_f = 34.6°$, and $|d_{zzz}| = 19$ pm/V (48×10^{-9} esu) for **1**. Similarly, the (resonantly enhanced) value of $|d_{zzz}|$ for **2** is ~110 pm/V (280×10^{-9} esu), with the predominant fraction of the second harmonic generated along this component. This may be compared with a peak on-resonant value of 450×10^{-9} esu for a stilbazole–silicone multilayer.[25]

Calculation of Orientation Parameters. The SHG coefficient d is described by eq 3

$$d(-2\omega; \omega, \omega) = Nf^{2\omega}f^{\omega}f^{\omega}\beta(-2\omega; \omega, \omega)P \tag{3}$$

Here d is proportional to the number density of active molecules (N), the hyperpolarizabilities of the molecules β, and the orientation parameter (P) that quantifies the polar alignment of the molecular ensemble.[26] The parameter P is equal to the average $\cos^3 \theta$, where θ is the angle of the principal molecular axis with the surface normal.[27] A resonance factor, defined by eq 4

$$R = \frac{3\omega_0^2}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \tag{4}$$

where ω_0 is the frequency of the first excited state of the molecule and ω is the frequency of the fundamental used in the SHG experiment, relates the electronic transitions to the frequencies of the fundamental and the second harmonic and accounts for the enhancement of the nonlinear response near resonance.[28] The proportionality factor between d and these various quantities contains local field factors that would have to be explicitly determined in order to obtain P from d. Alternatively, we may assume that these factors are similar for various materials containing related chromophores of similar polarity. Since there are examples in the literature of appropriately analogous materials to multilayers of **1** and **2**, on which both d and P have been determined, we can calculate P for our materials using eq 5, relating d and the factors which comprise it for two different materials

$$P = \frac{dN'\beta'P'R_dR'_\beta}{d'N\beta R'_dR_\beta} \tag{5}$$

where the primes refer to materials from the literature, and R_x/R'_x is the ratio of resonance factors needed to convert quantity x to a common fundamental frequency.

We have selected five materials for comparison with our own. Three are poled polymers whose order parameters were either determined independently or may be derived from the product of the molecular dipole moment and the poling field.[27] The others are Langmuir–Blodgett films with known order parameter. Relevant parameters for these and our materials are listed in Table 3. The apparent order parameter for multilayers of **1** is approximately 0.20, while that for the more flexible **2** is 0.16.

The value for **1** may be considered a lower limit, since β for **1** may be reduced by 10–20% compared to a typical dialkylamino sulfone azo dye because of the diminished donating ability of the piperazine ring and a further 10–20% because of the effect of the aminophenylphosphonic acid chromophore whose β moment is in the opposite direction versus the principal chromophore moment.[28,29]

It would be tempting to combine the orientation of the piperazine dye with the β of the cyanovinyl chromophore to maximize the optical nonlinearity of the system. We did perform a crude synthesis of **12** but never observed an SHG signal from this compound deposited on a zirconated substrate. Concerned that the compound was decomposing under the deposition conditions (DMSO, 80 °C), we synthesized **11**, obtaining a sample pure by ^{1}H and ^{31}P NMR. We expect that **11** is chemically robust under the deposition conditions, and it formed a 20 Å monolayer. However, the UV–visible spectrum of this layer was broadened and 60-nm blue-shifted compared to the spectrum in DMSO, evidence of H-aggregation.[30] SHG was not observed from this monolayer.

The spectral shifting and nonlinear optical deactivation in monolayers of highly polar dyes has been observed previously and may arise from the large field that opposes the polarization that leads to SHG.[30] While shifts of only 20 nm (vs EtOH solution) were observed for **1**, it is still possible that d for this material was lowered by H-aggregation as well, especially in the best-ordered domains.

Taking into account that d for **1** used in eq 2 may have been an underestimate because of aggregation and that β for **1** was an overestimate, P for **1** is probably close to 0.3, implying a tilt angle of 45–50°. Neither aggregation nor an overestimated β are considerations for **2**, so its order parameter is decidedly lower than that of **1**. In either case, the observed tilting is puzzlingly inconsistent with the excellent correlation between the ellipsometric thickness per layer and the presumed length of the molecules. The tilting is consistent, however, with the lack of UV dichroism and X-ray diffraction and other manifestations of imperfect order in zirconium phosphonate surface multilayers.[31] The order parameter is also similar to what is observed in well-poled polymers[19,27] and many LB films, though not as good as the best LB films or favorable crystal morphologies,[3] where the enthalpy of association and the lack of molecular mobility during condensation of the material constrains the molecules to pack densely and in parallel.

Conclusions

Our method of synthesizing polar, self-assembled zirconium phosphate/phosphonate multilayers as second order nonlinear optical materials has been generalized to include several different chromophores. The new compounds produce films that are stable to solvents above at least 80 °C and do not lose activity if a nonpolar chromophore is inserted during the deposition sequence. The polar order of the films is greater using a rigid chromophore than with a more flexible one. However, activity can be lost through H-aggregation if the component molecules are both highly ordered and very dipolar. We hope to study the effects of electron donors and acceptors in neighboring layers on the nonlinear optical properties of the polar chromophore layers and also search for novel photorefractive and electrochromic effects in heterostructures of this type.

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