Figure 3 was released only during the oxidation of the polymer, indicative of Na^+ popping.

The experimental evidence presented above demonstrates that the self-doped polymers (P3-ETS and P3-BTS) act as cation ejectors during oxidation and proton absorbers during reduction. The proposed doping mechanisms (H^+-popping and Na^+-popping, respectively) have thus been confirmed. The acid and sodium forms of these 3-substituted polythiophene derivatives can therefore be considered as potential-dependent proton and sodium exchangers. The usefulness of the potential dependent proton exchange is currently limited by the normal ion exchange which is slower than the potential dependent one but still significant. It may be possible to control the amount of normal exchange by variations in electrolyte and medium, a part of ongoing studies.

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Evidence for Water Coordinated to the Active Site Iron in Soybean Lipoxygenase-1[1]

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In this communication I report evidence for the existence of at least one iron-coordinated water in the active site of soybean lipoxygenase-1. Lipoxygenases are atypical mononuclear nonheme iron dioxygenases that catalyze the peroxidation by dioxygen of fatty acids containing a 1,4-diene unit.[2] In contrast to the more familiar intradiol catechol dioxygenases, soybean lipoxygenase-1 contains an iron with a relatively high reduction potential[3] and no phenolate ligands. Although the fatty acid may bind very close to the iron,[4] there is no evidence for coordination of either the fatty acid or dioxygen to the metal.[5] Available data are consistent with a mechanism involving oxidation and deprotonation of the diene, yielding a radical species that may react directly with dioxygen.[6] This oxidation reaction would not require coordination of the substrate to the iron; however, the observed regio- and stereospecificity of the reaction might imply the existence of an iron–alkyl intermediate.[7] Thus, it is of considerable interest to know if the iron in lipoxygenase contains ligands that might be displaced by the substrate, an intermediate, or an appropriately designed inhibitor.

Mammalian lipoxygenases are the targets of active inhibitor design programs by virtue of their importance in the biosynthesis of leukotrienes.[8] One approach to such inhibitors is via substrate analogues with potentially iron-coordinating moieties.[9] Detailed structural information to support this approach has been lacking; it has been known only that the iron in ferrous soybean lipoxygenase-1 is six-coordinate,[10] probably with four imidazole ligands,[11] and that the protein-derived ligands in ferric lipoxygenase–catecholate complexes likely are three neutral and one anionic.[12] By comparison, the more thoroughly characterized active site iron in the intradiol catechol dioxygenases is known to contain water ligands that are displaced by substrate.[13]

Table I. Line Widths in the EPR Spectrum of Ferric Lipoxygenase at pH 7

		FWHH[a]		
	feature (g_y)	$H_2{}^{16}O$	$H_2{}^{17}O$	broadening
no addition[b]	7.3	71.9 ± 0.6	75.0 ± 0.7	3.1 ± 1.0
	6.4	65.8 ± 0.9	71.3 ± 0.3	5.5 ± 0.9
ethanol[c]	6.3	63.8 ± 1.1	70.6 ± 1.1	6.8 ± 1.5
HCN	6.4	72.6 ± 0.3	77.0 ± 0.3	4.4 ± 0.5

[a] Full width at half-height in g ± standard deviation in multiple measurements. [b] Four samples. [c] Three samples.

The EPR spectrum of ferric soybean lipoxygenase-1[14,15] at pH 7 comprises two major components, each typical of high-spin Fe^{3+} and each representing a ground-state Kramer's doublet of an $S = 5/2$ system: one shows features at $g = 7.3$, approximately 4.5, and 2 ($E/D \approx 0.06$),[16] while the other has features at $g = 6.4$, 5.7, and 2 ($E/D \approx 0.01$). In samples prepared in $H_2{}^{17}O$, the low field features of each component (g_y and g_x) show line-broadening that presumably arises from unresolved hyperfine coupling between the ^{17}O nucleus of bound water and the electronic spin (Table I).[17] Thus the iron sites represented by each of these components apparently have at least one exchangeable water ligand.

Unresolved hyperfine broadening from $H_2{}^{17}O$ is also observed in samples of ferric lipoxygenase-1 treated with either 8 mM ethanol or 5 mM cyanide at pH 7 (Table I). Addition of ethanol or KCN (at pH 7, effectively HCN) results in the appearance of a single major component in the EPR spectrum,[12] with features corresponding to $g = 6.3$, 5.8, and 2 or 6.4, 5.8, and 2, respectively, although neither of these species is thought to coordinate the iron.[18] Thus, although both ethanol and cyanide bind to lipoxygenase and affect the electronic structure of the iron, neither appears to cause the loss of all (if any) of the water from the iron.[19]

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At pH 9, where the enzyme is most active, ferric lipoxygenase exhibits an EPR spectrum with components similar to those seen at pH 7, although the ratios of intensities differ and the lines are considerably broader.[12] Addition of ethanol results in a single major component with apparent g values of 6.2, 5.8, and 2. Small line broadenings were observed in the presence of $H_2{}^{17}O$ before and after addition of ethanol, but quantitation was frustrated by the 120 G line widths.

This report presents evidence for at least one coordinated water (or hydroxide) at the iron site in ferric soybean lipoxygenase-1. This water is not displaced by ethanol or HCN, both of which affect the electronic structure of the iron. However, there is no significant line-broadening from $H_2{}^{17}O$ in spectra of the nitrosyl complex of ferrous soybean lipoxygenase-1;[4] either no water is coordinated to the iron in that complex, or the bound ^{17}O nucleus is only weakly coupled to the electron spin. Coordination of NO may displace water, or the water may be a ligand only in the oxidized enzyme. That point, the quantitation of the number of waters bound, and the extension to enzyme–inhibitor and enzyme–product complexes are being pursued currently by electron nuclear double resonance spectroscopy.

Water usually is assumed to be a readily displaceable ligand. The observation of water coordinated to the iron leaves open the question of whether the substrate or any intermediate of the reaction does bind to the iron and encourages the effort to design lipoxygenase inhibitors based on iron coordination chemistry.

Inclusion Tuning of Nonlinear Optical Materials: Switching the SHG of *p*-Nitroaniline and 2-Methyl-*p*-nitroaniline with Molecular Sieve Hosts

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Inclusion of a guest species into a host framework can be used in a combinatorial or synergistic mode to create nonlinear optic properties which are dramatically different from those of either host or guest independently. Molecular dipolar alignment has been observed in organic and organometallic host–guest chemistry where, for example, *p*-nitroaniline (NA, SHG = 0 due to its centrosymmetric crystal structure) in β-cyclodextrin has an SHG = 64 x quartz.[1] Inclusion chemistry can also be used to modify wave mixing and wave guide characteristics as illustrated by the use of ion exchange in the potassium titanyl phosphate (KTP) family.[2]

These observations and the fact that nonlinear optical properties are particularly sensitive to structural variations[3,4] suggest that inclusion chemistry can be used as a means for achieving fine control, through careful synthetic choices, of a variety of nonlinear optical effects. This paper gives the first report of the use of inorganic hosts and organic guests to form nonlinear optic materials. An SHG signal ten times larger than that of any previously reported organic or organometallic inclusion complex is observed.

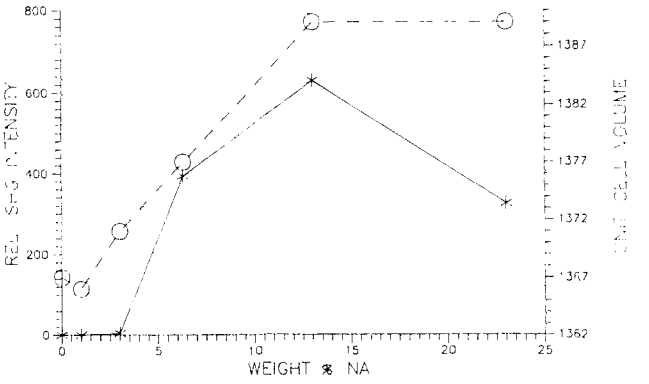

Figure 1. *p*-Nitroaniline in ALPO-5. Loading level (weight % NA) versus SHG intensity relative to quartz (solid line, *) and unit cell volume in Å^3 (dashed line, O).

Second harmonic generation (SHG) requires noncentrosymmetric structural features[3,5] which can be imposed on a sorbate by an acentric host or created by sorbate–host interactions. Many zeolites have ideal pore dimensions for the ordering or alignment of aromatic sorbates such as NA, and some have acentric structures. NA and 2-methyl-*p*-nitroaniline (MNA, SHG = 375[6]), which have similar second order molecular hyperpolarizabilities,[7,8] were introduced into a variety of acentric and centrosymmetric zeolite hosts by a vapor-phase loading method.[9] Loading levels are easily varied by this method up to a maximum at which pore-filling occurs. The guest molecules are strongly adsorbed. Heating to 100 °C under dynamic vacuum does not result in appreciable weight loss below the pore-filling level specific to each host–guest pair. The samples have a uniform bright yellow or yellow-orange color which pales slightly as the loading is lowered. Exposure to ambient air does not cause displacement of adsorbed organic from the molecular sieve pores according to X-ray powder diffraction pattern, which shows peaks due to the organic only when the pore capacity of the zeolite is exceeded.

NA in zeolites Y, Omega, and Mordenite[10] shows no SHG.[11] These are all centrosymmetric molecular sieves.[12] Figure 1 on the left-hand axis shows the SHG results for NA in ALPO-5,[10] an acentric (space group *P6cc*) molecular sieve with a neutral framework composed of alternating AlO_4 and PO_4 tetrahedra linked by oxygen bridges forming an array of one-dimensional 12-ring channels.[13] The SHG is near zero up to 3 wt % loading and then rapidly increases to a maximum of 630 at 13 wt % NA. This maximum is ten times larger than for any NA–organic host complex. SHG intensity tapers off at higher loadings due to dilution with external NA. Changes in unit cell volume with

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