Chapter 12

Nonlinear Optical Ionic Liquids

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Molecular orbital calculations indicate that molecules with a high
electron density diffused over a large volume will have
tertiary nonlinear optical activity. Anions often have
higher second hyperpolarizability values (gamma) than
similar neutral molecules. Also, molecules or ions containing
higher row elements have higher gammas. Salts with cations
that have their positive charge only weakly interacting with
the anion also enhance the tertiary nonlinear optical
activity. That looks like the recipe for ionic liquids. A
number of sulfur-containing mono- and dianion salts were
synthesized and characterized through Z-scan measurements.
Most were ionic liquids, and some showed significant tertiary
nonlinear optical behavior. The general features of
ionic liquids such as wide liquidus range, good thermal
stability, and low vapor pressure are particularly advantageous for applications of nonlinear optical materials.
Potential applications are in optical limiting and other all-
optic devices.
Introduction

The terms "nonlinear optics" and "ionic liquids" are not often mentioned in the same sentence. Here we describe some new materials that combine some of the favorable physical properties of ionic liquids with the potentially useful optical properties of third order nonlinear optical materials. A complete understanding of nonlinear optics (NLO) is not necessary to appreciate the interesting applications for NLO materials. A relatively superficial treatment of the appropriate optical properties, parameters and phenomena will be presented below. The niche for ionic liquids in the NLO materials field will be identified, and the preparation and properties of some remarkable ionic liquids that fill the niche will be described.

Others have shown that some organic salts exhibit nonlinear optical behavior. Some are second order (also called quadratic) nonlinear optical materials, such as the dihydrogen phosphate–organic cation salts described by Seddon and coworkers (1), and the stilbazolium BF₄⁻, triflate, and tosylate salts of Seth Marder and coworkers (2). These are all necessarily solids. Reports of third order (also called cubic) nonlinear optical organic salts are much rarer. Some recent examples are silver phenylacetylide, where the NLO effect comes from the anion (3), and arylidonium triflate salts, where cations are NLO active (4). Some of these latter salts actually meet the "boiling water" definition of an ionic liquid, but all are solids at room temperature.

Compounds with second order NLO activity must be non-centrosymmetric at both the molecular and materials level. Odd order (in practice just first and third) NLO materials have no symmetry restrictions at either the molecular or materials level. So it would seem easier to design and prepare third order compounds, and they could be liquids or solids. Our approach was to predict some anion structures that might have third order NLO activity, attempt to prepare some ionic liquids with these anions, and characterize the resulting compounds chemically, physically, and optically.

Nonlinear Optics of Molecules and Materials

A rigorous treatment of nonlinear optics is outside the scope of this chemistry paper. See one of the many monographs in this area for background reading (5). However, a somewhat superficial introduction to nonlinear optics is needed to describe the measured optical properties, and also to appreciate some useful applications of these nonlinear optical ionic liquids. The
polarization of a material may be described at the molecular (or ion) level by Equation 1, or at the macroscopic (or materials) level by Equation 2.

\[ \mu = \mu_0 + \alpha \cdot \mathbf{E} + \mathbf{\beta} : \mathbf{E} \mathbf{E} + \gamma : \mathbf{E} \mathbf{E} \mathbf{E} + \cdots \]  
(1)

\[ \mathbf{P} = \mathbf{P}_0 + \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} : \mathbf{E} \mathbf{E} + \chi^{(3)} : \mathbf{E} \mathbf{E} \mathbf{E} + \cdots \]  
(2)

For the molecular polarization, Equation 1, \( \alpha \) is the polarizability, \( \beta \) is the first hyperpolarizability, and \( \gamma \) is the second hyperpolarizability. The polarizabilities are properties of individual molecules or ions, so they can in principle be calculated from knowledge of the structure. For the macroscopic polarization, Equation 2, \( \chi^{(n)} \) is the \( n \)-th order susceptibility tensor. The values for the susceptibilities are properties of a material that can be measured experimentally, and are directly related to the molecular polarizabilities.

Two measurable third-order NLO properties are \( n_2 \), the nonlinear index coefficient and \( \alpha_2 \), the two-photon absorption (TPA) coefficient. These coefficients are related to the complex third-order NLO susceptibility through its real and imaginary parts, as shown in Equation 3(6, 7).

\[ n_2 = \frac{3\pi}{2\eta_0} \text{Re} \{ \chi^{(3)} \} \]

\[ \alpha_2 = \frac{3\omega}{2\varepsilon_0 \eta_0^2 c^2} \text{Im} \{ \chi^{(3)} \} \]  
(3)

\( \eta_0 \) is the index of refraction, \( \varepsilon_0 \) is the free space permittivity, \( c \) is the speed of light in vacuum, and \( \omega \) is the optical frequency. We used the z-scan method in order to determine experimentally the coefficients \( n_2 \) and \( \alpha_2 \). In this experiment, a laser beam was focused with a lens and the material under study moved across the focal plane in the direction of the beam propagation, say \( z \)-axis. The material experienced varying intensities, first increasing, as it got closer to the focal plane of the lens, and then decreasing past the focal plane. If \( n_2 \) is positive, the beam at a plane further down the propagation axis will expand making the intensity on that plane smaller at the "closed detector." As the material is moved past the focal plane, the beam will be focused tighter making the intensity at the plane larger. If \( n_2 \) is negative the reverse intensity behavior is observed. Similarly, if the whole beam at the observation plane is measured at the "open detector," as the material is scanned across the focal plane there will be a dip in intensity output as the absorption increases as the material then becomes dark.

We specifically applied the materials to light linearly polarized light, then measured the two-photon light.

To measure the material's properties, we first built a setup that allowed for light linearly polarized through the material. Two sets of light linear polarizers were used, one to helically rotate the polarization of the light, and the other to linearly rotate the light. We then used a photodiode to measure the light intensity as a function of time. The output from the photodiode was then measured as a function of distance, and the integral of the output was taken to obtain the intensity as a function of distance. The intensity as a function of distance was then used to determine the nonlinear index coefficient and the two-photon absorption coefficient. Molecules (or ions) can be excited by electric-field-induced transitions, and the calculated yield approaches the relative third-order nonlinear susceptibility.
material traverses the focal plane. The nonlinear absorption coefficient $\alpha_2$ can then be determined from the size of the intensity dip. It can easily be imagined that the dip in the intensity is located at the inflection of the previous description, where the intensity went from minimum to a maximum as a function of $z$ before flattening out again. The two coefficients can be related through the Kramers-Kronig relations, or dispersion relations.

We are interested in the third-order optical properties of our materials. Specifically, we wish to use third-order NLO ionic liquids for light limiting applications, where the relevant third-order NLO effect is TPA. These materials show TPA effects and may be used as light limiting because at low intensities ("low" means everyday normal light intensities) the material absorbs light linearly according to Beer's Law. However, at high intensities (e.g., laser light) the absorption increases with intensity. A material that is an effective two photon absorber will be effective for eye and sensor protection from laser light.

To meet our goals the optimization of the optical limiting properties of a material should correspond with maximizing the third-order NLO properties. For both second-order and third-order NLO behavior, materials are typically built starting at the molecular level, which are engineered with strong electron donating groups tethered to a strong electron acceptor group via an extended $\pi$-conjugated system. There have been numerous reports of optimizing the polarizability of these molecules though increasing the length of the conjugation, as well as increasing the electron-directing effect of the functional groups attached to the chain (8).

**Prediction of Nonlinear Optical Activity**

Molecular orbital computational methods predict properties of molecules (or ions) quite well. It is more difficult to predict materials properties, so we calculated $\gamma$, the second hyperpolarizability, to serve as an indicator of the relative third order responses of candidate materials for light limiting.

In an attempt to develop a diffuse Gaussian basis set usable for the *ab initio* calculation of the second hyperpolarizability ($\gamma$) of molecules of technologically important size, we noted that $\gamma$ was quite sensitive to the inclusion of diffuse functions in the basis set, but insensitive to the quality of the valence portion of the basis set. This observation indicated that the region of the electron density farthest from the nuclei, the "diffuse" region, generated the bulk of the second hyperpolarizability. The diffuse region contains those electrons least strongly bound to the molecule. It would seem reasonable then that an increase of the electron density in this region would lead to an increase in $\gamma$. Three methods to
The calculations on these structures point to general types of anions that may have good third order nonlinearity, but of course real materials must also contain cations. The high charge density of small cations can decrease the polarizability of the diffuse anions, as demonstrated in Table II. The obvious approach to avoiding this effect is to employ cations that have the positive charge delocalized or screened from the anion by molecular foliage. Salts with large organic cations are often ionic liquids.

### Table II. Effect of Cations on Diffuse Anion Second Hyperpolarizability

<table>
<thead>
<tr>
<th>Cation</th>
<th>$\gamma \times 10^4$ a.u. (RHF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>268</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>42</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>71</td>
</tr>
<tr>
<td>K$^+$</td>
<td>119</td>
</tr>
</tbody>
</table>

### Ionic Liquids

The use of an ionic liquid may have some major advantages as light limiting materials. The low volatility, high thermal stability, and relatively easy preparation are all favorable for sensor protection. However, the fact that ionic liquids are viscous liquids is the most disadvantageous property. When two photon absorption functions as it should during irradiation of high intensity laser light, the material necessarily absorbs considerable energy. We saw the consequences when we used laser pulses that were too long during the Z-scan measurements of optical response (*vide infra*). When a lot of energy is
deposited in a small volume the ionic liquid does thermally decompose, producing a black char. The advantage of using a liquid film is that the decomposition products can diffuse away or the charred area can be removed by convective flow.

The calculations guide us to compounds that have heavy anions with delocalized electrons combined with large non-polarizing cations. Our experience tells us that many salts with such structures are liquid at or near room temperature. 1-Ethyl-3-methylimidazolium was the initial cation chosen for this study, but had to be abandoned due to the acidity of that cation and the basicity of the sulfur-containing anions. The cation used in all of the ionic liquids reported below is tetradecyl(triethyl)phosphonium, which we will abbreviate as [PR₄].

\[
\begin{align*}
\text{tetradecyl(triethyl)phosphonium, [PR₄]} \\
\end{align*}
\]

Some physical properties, the linear absorption, and the third order nonlinear optical response were measured. The method used for the nonlinear optical characterization was Z-scan, which detects the focusing of a laser beam by the intensity dependent refractive index of the material. The Z-scan experiments are the most difficult to do, and not all of the ionic liquids that we prepared have been optically characterized yet. The density, viscosity, melting or glass transition temperature, maximum linear absorption wavelength, and linear molar absorptivity are given in Table III. Some of the ionic liquids are not expected to be NLO active, but were prepared and characterized for comparison purposes.

Some of the anions in Table III are not exactly the same as the models we used to predict the gammas in Table I. We did not calculate two of the anions ([Co(NCS)₄]²⁻ and [CoCB]¹), because they we synthesized faster than they were calculated. The structures of anions in Table II that are not shown below Table I are.
Table III. Physical and Optical Properties

<table>
<thead>
<tr>
<th>anion</th>
<th>$T_\text{g}$ $^\circ\text{C}$</th>
<th>$T_\text{dec}^a$ $^\circ\text{C}$</th>
<th>Density $^b$ g/cm$^3$</th>
<th>Viscosity $^b$ $\eta$ cP</th>
<th>$\lambda_{\text{max}}^c$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3dmn]$^2^-$</td>
<td>-71</td>
<td>360</td>
<td>0.942</td>
<td>4780</td>
<td>394</td>
</tr>
<tr>
<td>[K-salt]$^2^-$</td>
<td>-79</td>
<td>350</td>
<td>0.960</td>
<td>560</td>
<td>396</td>
</tr>
<tr>
<td>[ddtc]$^-$</td>
<td>-77</td>
<td>255</td>
<td>0.942</td>
<td>1470</td>
<td>305</td>
</tr>
<tr>
<td>[xan]$^-$</td>
<td>-70$^e$</td>
<td>290</td>
<td>0.920</td>
<td>1480</td>
<td>345</td>
</tr>
<tr>
<td>[N(CN)$_2$]$^-$</td>
<td>-67</td>
<td>395</td>
<td>0.904</td>
<td>490</td>
<td>$d$</td>
</tr>
<tr>
<td>[T$_6$N]$^-$</td>
<td>-76$^e$</td>
<td>400</td>
<td>1.080</td>
<td>450</td>
<td>$d$</td>
</tr>
<tr>
<td>[Co(NCS)$_4$]$^2^-$</td>
<td>-72$^e$</td>
<td>405</td>
<td>0.963</td>
<td>2436</td>
<td>628</td>
</tr>
<tr>
<td>[CoCB]$^+$</td>
<td>-71</td>
<td>440</td>
<td>1.000</td>
<td>3702</td>
<td>290</td>
</tr>
</tbody>
</table>

a. TGA onset temperature  
b. At 20$^\circ$ C  
c. Neat liquid in 10µm pathlength cell  
d. Colorless  
e. Melting temperature; not glass transition

![Chemical structures]

The same as the models we calculated two of the anions decomposed faster than they were not shown below Table.
The metal-containing anions were of interest for NLO applications in that they contain diffuse σ-orbitals, they can be easily functionalized and tuned based on the ligand systems, and their total negative charge can be built up rapidly with appropriate ligands. Additionally, the cobalt bis(dicarboxylide), CoCB, has boron-carbon cages which are σ-aromatic, thus providing the delocalization desired for high NLO behavior. One potential flaw with these metal-ligand systems is that the central metal cations are typically in the +2 or greater oxidation state, potentially concentrating the charge of the ligands adjacent to the metal. However, at the molecular level, this may not be the case as the molecular orbitals will differ significantly from the formal charges designated to the atomic components. There have been previous reports (12,13) of solutions or solids of the metal complexes similar to the metal-containing salts displaying NLO behavior, which provided motivation to choose these unions to develop into RTILs.

The preparation of the somewhat complicated looking ionic liquids is actually quite easy. The chloride salt of the tetradecyl(trihexyl)phosphonium cation is commercially available as CYPHOS IL 101. The sodium salts of the thiolate anions are all prepared by variations on the general addition reaction in Equation 4.

\[ \text{Na}^+ \text{A}^- \text{X}^- + \text{CS}_2 \rightarrow \text{Na}^+ \text{A}^- \text{X}^- \text{CS}^- \]

where X is a nucleophilic atom and A is the rest of the molecule. The sodium salts are then used to create the desired salt by a metathesis reaction with the tetradecyl(trihexyl)phosphonium chloride. Other large tetraalkyl phosphonium halides are also available, and they also combine with the large anions to form ionic liquids. See the experimental section for the details of the syntheses.
Figure 2. Z-scan experiment on [PR$_3$]$_2$(Co(NCS)$_2$] with the transmittance recorded at the open detector.

Table IV. Nonlinear Optical Properties

<table>
<thead>
<tr>
<th>Anion</th>
<th>Wavelength nm</th>
<th>$n_2$ measured $\times 10^{-14}$ m$^2$ W$^{-1}$</th>
<th>$\alpha_2$ measured $\times 10^{-11}$ m W$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[xan]$^-$</td>
<td>910</td>
<td>-0.99</td>
<td>0$^a$</td>
</tr>
<tr>
<td>[CoCB]$^-$</td>
<td>910</td>
<td>-0.22</td>
<td>0$^b$</td>
</tr>
<tr>
<td>[ddtc]$^-$</td>
<td>910</td>
<td>-0.45</td>
<td>0$^a$</td>
</tr>
<tr>
<td>[Co(NCS)$_2$]$^{2-}$</td>
<td>910</td>
<td>-1.9</td>
<td>0$^b$</td>
</tr>
<tr>
<td>[dtmn]$^{3-}$</td>
<td>910</td>
<td>-6.1</td>
<td>8.4$^a$</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>1064</td>
<td>0.0003</td>
<td>0$^a$</td>
</tr>
<tr>
<td>ZnSe</td>
<td>532</td>
<td>0.0007</td>
<td>5.8$^a$</td>
</tr>
</tbody>
</table>

a. Low laser power used
b. Not yet determined

Synthesis of Ionic Liquids

Alkali metal salts of aromatic or easily synthesized diethylthiocarbamate, (Fluka), lithium bis(triethyloxyl)phosphine oxide, and cesium bis(dicarbollyl) oxide were received. Sodium nitrothiocarbonate, K$_2$[SbF$_5$], and [NH$_4$][SCN] were dissolved in methanolic NaOH with tetrathiooxamocobaltate(II) under high vacuum. To prepare the ion, a reaction solution of [xan], [N(CN)$_2$], [T$_5$N], CHCl$_3$ solutions of the [xan]. [T$_5$N] were washed several times with water to form the resulting ionic liquid, which was then vacuum distilled at 75-85°C.

Properties of Ionic Liquids

Thermal gravimetric analysis (TGA) was performed on SDT 2960, and different samples were heated at 5°C/min on a TA instrument. Indium and aluminum were used as reference materials and provided with the instrument.
Experimental

Synthesis of Ionic Liquids

Alkali metal salts of the desired anions were either commercially available or easily synthesized through known reactions. Sodium diethylthiocarbamate, Na[ddtc] (Fischer), sodium dicyanamide, Na[N(CN)$_2$] (Fluka), lithium bis(trifluoromethane)sulfonamide, Li[Tf$_2$N] (Aldrich), and cesium bis(dicarboxyl)coaltar(III), Cs[CoCB] (Katchem, Czech.) were used as received. Sodium dithiomalononitrile, Na$_2$[dtmn]$_2$, and potassium nitrotriacetate, K$_2$[K-salt], were prepared as previously reported (15,16). Sodium methylxanthate, Na[oxan], was prepared through the reaction of 1.2 eq. methanolic NaOH with 1 eq. carbon disulfide in methanol. Ammonium tetraethiocyanocobaltate(II), [NH$_4$]$_2$[Co(NCS)$_4$], was prepared from 4.2 eq. of [NH$_4$][SCN] and 1 eq. of CoCl$_2$ in H$_2$O, and the product was not isolated before proceeding to the following metathesis reaction to make the ionic liquid.

To prepare the ionic liquid materials, the above alkali metal salts were used in metathesis reactions with an appropriate number of equivalents of the tetradecyl(triethyl)phosphonium chloride, CYPHOS 101 (Cytec), in organic solvents. Typically the alkali salts were water soluble, including the [ddtc], [xan], [N(CN)$_2$], [Tf$_2$N], and [Co(NCS)$_4$] salts. These salts were stirred with CHCl$_3$ solutions of the CYPHOS for 24 hours, separated and the organic layer washed several times with water and then evaporated off. Exceptions to this are the [CoCB] salt, which was reacted with CYPHOS in THF; and the [dtmn] and [K-salt] were reacted with CYPHOS in EtOH. In these cases, the alkali chloride by-product could be filtered out, the organic solvent evaporated, and the resulting ionic liquid purified through redissolving in CHCl$_3$ and washed with water several times. All of the resulting ionic liquids were dried under vacuum at 75-85°C.

Properties of Ionic Liquids

Thermal gravimetric analyses were run at 10°/min on a TA Instruments SDT 2960, and differential scanning calorimetry (DSC) was performed at 5°C/min on a TA instruments DSC 2910. The TGA instrument was temperature calibrated from room temperature to 800° at 10°/min. using indium and aluminum. It was weight calibrated with ceramic standards provided with the instrument. The DSC instrument was calibrated using
to be 1.5-2.0 GW/m². All of the measurements were performed at room temperature.

Conclusions

Ionic liquids with good third order nonlinear optical properties may be designed and prepared. Measurements show that the $\chi^{(3)}$ of the actual materials have a similar relative ordering to the molecular $\gamma$ predicted by theory.

References

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