

# A Systematic Method for Using Structural and Numeric Databases To Choose Compounds of Potentially High Nonlinear Optical Susceptibility

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We are testing the hypothesis that commercial, on-line databases in the physical sciences can provide a rapid, inexpensive way to explore materials space. We chose to investigate the nonlinear optical properties of organometallic compounds because of the technological interest in nonlinear optical materials and the molecular design possibilities in organometallics. We found that although the data are too limited to answer some questions, the process holds the promise of becoming a useful tool. Using structural and property data in Gmelin Online, such as crystal space group, dipole moment, substructure, and ligand linearized structure, we found several compounds that warrant further consideration as nonlinear optical materials.

## INTRODUCTION

The advent of commercially available, on-line databases in the physical sciences offers us the new possibility of being able to rapidly and inexpensively explore materials space for substances with specific properties. While structural databases are used with great sophistication by toxicologists and chemists in the pharmaceutical industry to predict chemical and biological activity, the use of structural and properties databases is much less common and sophisticated among materials scientists. Our long-term objective is to see if structural and properties databases can be used to predict materials properties with a reasonable degree of success.

Databases such as Beilstein Online, Gmelin Online, and Crysdat combine numerical and structural data in ways that could speed the development of new materials. For example, Gmelin Online contains structures and critically evaluated data from the *Gmelin Handbook of Inorganic and Organometallic Chemistry* for over 500 000 materials in 120 different data fields such as crystal space group, dipole moment, electrochemical potential, and UV and visible spectra. As a first step, we have embarked on a project to see if we can use numerical databases to choose compounds that have a high probability of showing nonlinear optical (NLO) tendencies. In this paper, we report on our attempts at choosing good screening strategies. Being information scientists rather than solid-state physicists or chemists, our goal was to explore the possibilities in the method, not necessarily to find superior NLO materials.

We chose to begin our work with nonlinear optical materials because of the wide range of factors affecting their performance and widespread interest in their potential use in telecommunications, optical data storage, and optical information processing applications. Our specific interest in organometallic compounds stems from predictions that they might provide fertile ground for a structure versus optical property investigation,<sup>1</sup> a desire to start with a relatively small set of compounds, and a realization that the nonlinear optical properties of organometallics have been widely studied only in the last few years. In the interest of simplicity, the only nonlinear optical property we considered was second harmonic generation (SHG).

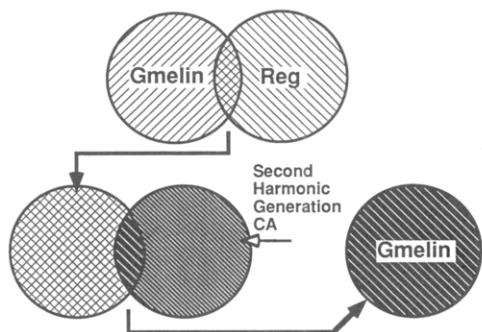
Nonlinear optics have been the subject of many investigations over the past 30 years. The physics of nonlinear optical processes was extensively studied in the 1960s and 1970s.<sup>2</sup>

Inorganic solids were studied first, and the nonlinear optical properties of many are known. More recently, organic materials have become popular subjects for investigation because of their fast response times, lower dielectric constants, and better processability. At Lawrence Livermore National Laboratory (LLNL), the main interest has been in finding materials to convert laser light to the shorter wavelengths that are desirable for inertial confinement fusion.<sup>3-7</sup> Use of the Crysdat database was a feature of these investigations. The search for new organic NLO materials has been extensively reviewed.<sup>8-11</sup> The best second harmonic generator found to date is the organic compound 3-methyl-4-methoxy-4'-nitrostilbene (MMONS), which has an NLO response 1250 times that of urea.<sup>12</sup> In the late 1980s, organometallic compounds attracted the interest of materials scientists because they can have conjugated  $\pi$ -electron systems or low-lying charge-transfer excited states that promote SHG and a range of oxidation states and ligand environments that can offer flexibility in the design of promising molecules.<sup>13-15</sup> Useful nonlinear optical activity is known to result from a combination of bulk and molecular properties: noncentrosymmetry, high hyperpolarizability, proper phase matching, and transparency in a usable region. In this paper, we will deal only with crystal symmetry and hyperpolarizability. In future papers, we hope to look at spectral and phase-matching considerations.

**Crystal Space Group.** A prerequisite for second harmonic generation is that the bulk material be noncentrosymmetric. Since crystal symmetry cannot be reliably predicted from molecular structure, crystallographic data are necessities if one is to develop a systematic method for predicting nonlinear optical tendencies. Of the known 230 crystal space groups, 101 are noncentrosymmetric. It has been estimated that only 10% of organic compounds crystallize noncentrosymmetrically and that most of the good organic SHG materials will come from the  $P2_1$  (4) and  $P2_12_12_1$  (19) crystal space groups.<sup>10</sup> While chirality in a molecule guarantees noncentrosymmetry in the crystal, it does not guarantee useful SHG. Seventeen percent of the inorganic and organometallic compounds in Gmelin Online crystallize noncentrosymmetrically.

**Hyperpolarizability.** Along with being noncentrosymmetric, a potential second harmonic generator must also be sufficiently hyperpolarizable. Hyperpolarizability can be described as the difference between the ground-state and excited-state dipole moments. A number of properties, including ground-state dipole moment, redox potential, and the electronic spectrum can provide clues to the hyperpolarizability of a

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**Figure 1.** Set of compounds that has been tested for SHG and is in Gmelin Online, found by using the LC field in the Registry file, registry numbers, and the concept-searching capability of CA.

material. Systems with extended  $\pi$ -conjugation are good systems for separating charge, so they are intuitively good candidates for SHG materials.

## RESULTS

**Known SHG Materials.** The first step in the project was to find all the compounds in Gmelin Online whose tendency to generate second harmonics had been measured. The first step was intended to give us an idea of how much numerical data was available on Gmelin Online and whether or not we could correlate it with the material's SHG. Concept searching on Gmelin Online is possible only by searching the rather limited controlled vocabulary. For example, it is impossible to search for second harmonic generation or nonlinear optical properties. In fact, the only searchable electrooptical effect is the Kerr effect. We circumvented this limitation by beginning the search in the STN Registry file and building a set of all the compounds for groups VI–VIII transition metals that had a Gmelin locator code (LC). The corresponding CAS registry numbers were crossed over to the CA file and combined with terms for second harmonic generation. The CAS registry numbers associated with these records were, in turn, selected and searched for in Gmelin Online (Figure 1). Using this technique, 34 materials were found. These materials and their SHG tendencies are listed relative to urea in Table I.

We may illustrate this approach by taking the example of rhenium. We know from searching the Registry file for records that combine the element code (ELS) for rhenium and the LC for Gmelin that, at the time of the search (fall of 1992), 2675 rhenium compounds in the STN Registry file were also in Gmelin Online. Our search of CA for occurrences of these 2675 CAS registry numbers associated with second harmonic generation turned up a single paper published by Calabrese and Tam in 1987.<sup>13</sup> This paper gave the CAS registry numbers for two rhenium compounds,  $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$  (**8**) and  $\text{Re}(\text{bpy})(\text{CO})_3\text{CF}_3\text{SO}_3$  (**11**). The Gmelin records were checked for pertinent data by searching the fields available (FA) field. Data for **8** and **11** were minimal, and the crystal structure for **11**, published by Tam and Calabrese,<sup>13</sup> was not in the database.

An interesting feature of Gmelin Online is the Gmelin practice of assigning multiple records to the same compound, a practice that has advantages and disadvantages for the user. Presumably, multiple records result from the Gmelin practice of assigning a new record to a compound when new structural data are obtained. For example, there are seven separate Gmelin records for  $\text{Ru}(\text{bpy})_3$ . Later on we shall see that multiple records for  $\text{Cr}(\text{CO})_3(o\text{-toluidine})$  proved enlightening. In the rhenium search, we turned up three separate records: two records for **8** and one for **11**.

**Table I.** Compounds Whose Nonlinear Optical Propensity Has Been Measured Relative to Urea

| no. | compound  | SHG                | csg <sup>a</sup> | ref |
|-----|---|--------------------|------------------|-----|
| 1   | (Z)-(1-ferrocenyl-2-(4-nitrophenyl)ethylene)  | 62                 | 43 <sup>b</sup>  | 14  |
| 2   | <i>trans</i> -Pt(PEt <sub>3</sub> ) <sub>2</sub> (Br)(2-CH <sub>3</sub> -4-NO <sub>2</sub> -Ph) | 14                 |                  | 28  |
| 3   | <i>trans</i> -Pd(PEt <sub>3</sub> ) <sub>2</sub> (Br)(2-CH <sub>3</sub> -4-NO <sub>2</sub> -Ph) | 10                 |                  | 28  |
| 4   | <i>trans</i> -Pt(PEt <sub>3</sub> ) <sub>2</sub> (I)( <i>p</i> -nitrophenyl)                    | 8                  | 36               | 28  |
| 5   | <i>trans</i> -Pd(PEt <sub>3</sub> ) <sub>2</sub> (Br)( <i>p</i> -nitrophenyl)                   | 7.2                |                  | 28  |
| 6   | <i>trans</i> -Pt(PEt <sub>3</sub> ) <sub>2</sub> (Br)( <i>p</i> -nitrophenyl)                   | 4.2                |                  | 28  |
| 7   | <i>trans</i> -Pt(PEt <sub>3</sub> ) <sub>2</sub> (Br)( <i>p</i> -benzaldehyde)                  | 3.4                |                  | 28  |
| 8   | $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$   | 3                  |                  | 13  |
| 9   | <i>trans</i> -Pd(PEt <sub>3</sub> ) <sub>2</sub> ( <i>p</i> -nitrophenyl)                       | 2.3                |                  | 28  |
| 10  | <i>trans</i> -Pd(PEt <sub>3</sub> ) <sub>2</sub> (Br)( <i>p</i> -benzaldehyde)                  | 2.3                |                  | 28  |
| 11  | $\text{Re}(\text{CO})_3(\text{bpy})\text{CF}_3\text{SO}_3$                                      | 2                  | 4 <sup>b</sup>   | 13  |
| 12  | <i>trans</i> -Pt(PEt <sub>3</sub> ) <sub>2</sub> (Br)( <i>o</i> -nitrophenyl)                   | 0.8                |                  | 28  |
| 13  | $\text{Cr}(\text{CO})_3(\text{styrene})$  | 0.7 <sup>c</sup>   | 19               | 17  |
| 14  | $\text{Mo}(\text{CO})_4(\text{bpy})$  | 0.5                |                  | 13  |
| 15  | <i>trans</i> -Pt(PEt <sub>3</sub> ) <sub>2</sub> (Br)( <i>p</i> -cyanophenyl)                   | 0.4                |                  | 28  |
| 16  | $\text{W}(\text{CO})_4(\text{bpy})$   | 0.3                |                  | 13  |
| 17  | $\text{Cr}(\text{CO})_4(\text{bpy})$  | 0.2                |                  | 13  |
| 18  | $\text{Cr}(\text{CO})_3(m\text{-anisidine})$  | 0.12 <sup>c</sup>  |                  | 17  |
| 19  | $\text{W}(\text{CO})_5(p\text{-benzoylpyridine})$   | 0.08 <sup>c</sup>  |                  | 17  |
| 20  | $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  | <0.01 <sup>c</sup> |                  | 17  |
| 21  | $\text{Co}(\text{acac})_3$  | detected           | 14               | 30  |
| 22  | $\text{Co}(\text{3-chloroacac})_3$  | detected           |                  | 30  |
| 23  | (tris(1-phenyl-1,3-butanedionato)cobalt)  | 0                  |                  | 30  |
| 24  | ( <i>S</i> )-1-ferrocenylethanol  | 0                  |                  | 31  |
| 25  | $\text{Cr}(\text{CO})_3(o\text{-methylbenzaldehyde})$   | 0                  |                  | 31  |
| 26  | $\text{Cr}(\text{CO})_3(\text{tetrahydronaphthalene})$  | 0                  |                  | 17  |
| 27  | $\text{W}(\text{CO})_5(p\text{-acetylpyridine})$  | 0                  |                  | 17  |
| 28  | $\text{W}(\text{CO})_5(p\text{-cyanopyridine})$   | 0                  |                  | 17  |
| 29  | $\text{Cr}(\text{CO})_3(o\text{-toluidine})$  | 0                  | 15               | 17  |
| 30  | $\text{Rh}(\text{CO})_2(\text{acac})$   | 0                  |                  | 32  |
| 31  | $\text{Rh}(\text{CO})(\text{PPh}_3)(\text{acac})$   | 0                  |                  | 32  |
| 32  | $\text{Rh}(\text{acac})_3$  | 0                  |                  | 30  |
| 33  | $\text{Ru}(\text{bpy})_3$   | 0                  |                  | 26  |
| 34  | ( <i>E</i> )-(1-ferrocenyl-2-(4-nitrophenyl)ethylene)   | 0                  |                  | 14  |

<sup>a</sup> Crystallographic space group number as taken from ref 46. <sup>b</sup> Not reported in Gmelin Online. <sup>c</sup> Reported relative to ADP and converted to relative to urea.

Data for the materials in Table I were generally scant. One reason was that, at the time of the search, records were still being loaded into the database, and there were gaps in the coverage. Crystal space group data were available for only four compounds. Two more crystal space groups, not present in Gmelin Online, were found in papers that the CA search turned up. Ground-state dipole moments were not available for any of the 34 compounds in Table I, and electronic spectra were available for only 11 compounds.

**Other Strategies.** Of the determinants of SHG that we described earlier, the one most difficult to predict or calculate is crystal symmetry. For that reason, we chose the set of materials represented in Gmelin that had noncentrosymmetric crystal space groups. Of the 500 000 records in the Gmelin database, 23 559 crystal space groups are reported. Of these, 4178 (17%) are associated with noncentrosymmetric space groups. In other words, the Gmelin database has 4178 compounds that meet the first requirement for SHG. Our strategy was to look for materials with known noncentrosymmetry that also had promise of high hyperpolarizability.

As has been stated, dipole moments can be clues, albeit complicated ones, to hyperpolarizability. Because dipole moments are included in the online Gmelin database, we looked for compounds with noncentrosymmetric crystal space groups and known dipole moments. Of the 1153 dipole moments reported in Gmelin, 35 are associated with noncentrosymmetric crystal space groups. Eight of the materials in this set of 35 have  $\pi$ -conjugated electron systems, and these are listed in Table II along with their crystal space groups and dipole moments.

**Table II.** Compounds in Gmelin That Crystallize Noncentrosymmetrically and Whose Ground-State Dipole Moments Are in the Database<sup>a</sup>

| no. | compound   | csg   | DM (D) | ref    |
|-----|--|-------|--------|--------|
| 35  | Cr(CO) <sub>3</sub> ( <i>o</i> -mesitylene)  | 19    | 5.46   | 33, 34 |
| 36  | Cr(CO) <sub>3</sub> ( <i>m</i> -mesitylene)  | 11, 4 | 5.39   | 33, 45 |
| 37  | Tc(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Cl   | 40    | 5.16   | 35     |
| 38  | Cr(CO) <sub>3</sub> (toluene)  | 19    | 5.12   | 36, 34 |
| 39  | Hf( $\pi$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ( $\sigma$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> | 113   | 3.76   | 19, 37 |
| 40  | Zr( $\pi$ -C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> ( $\sigma$ -C <sub>5</sub> H <sub>5</sub> )              | 19    | 3.56   | 20, 37 |
| 41  | Pd <sub>2</sub> (dichlorobis( <i>n</i> -Bu <sub>3</sub> P)oxalato)   | 4, 14 | 3.55   | 38     |
| 42  | Co <sub>2</sub> (CO) <sub>6</sub> (diphenylacetylide)  | 9     | 2.1    | 39, 40 |

<sup>a</sup> Where dipole moments were reported in ranges, we recorded the upper limit.

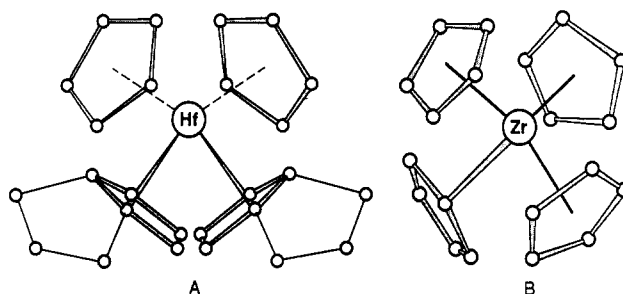
**Table III.** Styryl and Phenylacetylide Complexes That Have Noncentrosymmetric Crystal Space Groups

| no. | compound   | csg | ref |
|-----|--|-----|-----|
| 43  | <i>trans</i> -Rh(Me <sub>3</sub> P) <sub>3</sub> (H)(phenylacetylide) <sub>2</sub>       | 4   | 24  |
| 44  | Ru(C <sub>5</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (dimercaptoacetylide) | 19  | 41  |
| 45  | <i>trans</i> -Ru(2-acetato)(carbonyl)(phenylethenyl)(PPh <sub>3</sub> ) <sub>3</sub>     | 9   | 42  |
| 46  | tris(cinnamylidene- <i>p</i> -toluidine)(trifluoromethanesulfonate)-copper               | 146 | 27  |
| 47  | (dichlorobiscinnamylidene-2,4-dimethylpent-3-ylamine)-copper                             | 19  | 27  |
| 13  | Cr(CO) <sub>3</sub> (styrene)  | 19  | 29  |
| 48  | W(CO) <sub>5</sub> ( <i>N,N</i> -diethyl-2-methyl-3-phenylselenoacrylamide)              | 19  | 43  |
| 49  | ( <i>N</i> -(3-phenyl-1-(phenylethynyl)-2-propynylidene)-benzenamide)cobalt              | 19  | 44  |

Another way to look for SHG candidates relies on the chemical knowledge of the investigator and the substructure searching capabilities of the databases. The strategy consists of looking for materials that have noncentrosymmetric crystal structures and  $\pi$ -conjugated organic fragments. To this end, we searched for all the noncentrosymmetric compounds that had styryl or phenyl acetylenic structures. We found 2501 compounds with styryl fragments and 828 with phenylacetylide structures. Eight of these compounds were organometallic. They are shown in Table III.

The list of known materials with tendencies toward SHG (Table I) indicates that, next to the ferrocenyl compound, four-coordinate platinum group compounds are the strongest second-harmonic generators. Cheng et al. have discussed the nonlinear optical tendencies of square planar, metal aromatics in detail.<sup>15</sup> With this in mind, we searched for all the four-coordinate platinum-group compounds that have two donor ligands and noncentrosymmetric space groups. Gmelin Online provides a practical route for this strategy through the Ligand Linearized Structure Formula. We looked for all the compounds that have the metal(D)<sub>2</sub>(L)(X) structure, where D stands for donor, L for ligand atom carbon, and X for an acid ligand like halogen. We did this search for complexes of platinum, palladium, and nickel and found five answers. Of the five complexes, four were platinum-based and one palladium-based. All had one halogen and two phosphine ligands. One (4) had already been measured for SHG. The other compounds had either a carbon-metal  $\sigma$ -bonded ketene, pyridine, or indole group in the fourth position.

Cheng et al.<sup>15</sup> also report that low redox potential can be an indicator of hyperpolarizability. Gmelin Online has a searchable field for electrochemical cell potential (ecpot), which can be viewed as an oxidation potential. There are 2226 measured cell potentials in Gmelin. Combining cell potentials with the set of desirable crystal space groups gives 32 answers. However, all of these materials are inorganic crystals and do not fit within the somewhat narrow confines we set for this paper.

**Figure 2.** Tetrakis(cyclopentadienyl)hafnium (A) and tetrakis(cyclopentadienyl)zirconium (B), having noncentrosymmetric crystal space groups and relatively large ground-state dipole moments (from refs 19 and 20).

## DISCUSSION

**Known Nonlinear Materials.** The strategy of searching for and examining the properties of known second harmonic generators described in the Results Section turned up relatively few compounds and not enough data to make any quantitative generalizations about the properties that might point to promising new SHG materials. However, aspects of this search warrant further discussion.

Arranging the materials according to the magnitude of the SHG indicates that the ferrocenyl material is the best second harmonic generator by far and that the square planar palladium and platinum complexes are an interesting class of materials because so many are active. On the other hand, the arene metal carbonyl complexes show very little activity. Recent papers have commented at length on the theoretical aspects of this observation.<sup>15,16</sup> The simple view of this theoretical work is that good hyperpolarizability demands that the dipole moment be coincident with the  $\pi$ -electron system. This is clearly not true in the case of the arene metal carbonyls, where the highly electronegative carbonyl groups draw charge from the metal and form a dipole along the ring-metal axis perpendicular to the arene ligand.

As an interesting aside, the search in CA turned up Cr(CO)<sub>3</sub>(*o*-toluidine) (29) as a material with no measureable SHG.<sup>17</sup> When the registry number for 29 was crossed over to Gmelin, we found three Gmelin records. The Gmelin records represent the (+) enantiomer of *o*-toluidine, the (−) enantiomer, and the racemate. The resolution of the enantiomers was reported in 1970 in the *Rev. Roum. Chim.* in a reference that has never been cited.<sup>18</sup> Although the SHG was reported as zero, one can surmise that it was the racemate that was measured. Even though it is generally believed that arene metal carbonyls are not good SHG materials, the pure enantiomers would have to show some activity.

The data in Table II indicate that ground-state dipole moment values are valuable only when considered with structural data. Chromium tricarbonyls, which have the highest ground-state dipoles in the table, have been studied extensively and shown to have low SHGs. For example, Cr(CO)<sub>3</sub>(toluene) (38), which might seem to be an ideal choice from its crystal structure and large ground-state dipole moment, shows no tendency toward SHG. On the other hand, the cyclopentadienyl complexes of technetium, vanadium, hafnium, and zirconium, which have relatively high dipole moments and noncentrosymmetric space groups, are interesting in light of the finding by Struchkov et al. that tetrakis(cyclopentadienyl)hafnium (39) and tetrakis(cyclopentadienyl)zirconium (40) exist in distorted tetrahedrons (Figure 2) and have two and one  $\sigma$ -bonded cyclopentadienyl group, respectively.<sup>19,20</sup>

Although it falls outside of the limits of this paper, pentaphosphorus nitride dichloride turned up in the dipole search as an intriguing SHG possibility. This compound has a modest dipole moment of 0.48 D and crystal space group (csg) number 19.<sup>21,22</sup> Cyclic phosphorazenes have been known for a long time, and their structures and bonding studied extensively,<sup>23</sup> but, as far as we can tell, they have never tested for their nonlinear optical tendencies.

Structural searches yielded a diverse group of materials. The materials found by searching structural fragments and csg's turned up the eight materials in Table III. These include the previously measured Cr(CO)<sub>3</sub>(styrene) (no SHG) and an interesting hydridoacetylide complex of rhodium (43). It has been noted that acetylide moieties trans to each other should allow intramolecular charge transfer, especially if they incorporate donor and acceptor substituents. Such materials should be promising candidates for SHG.<sup>24</sup> In a more recent paper on the subject, Marder et al. have reported weak SHG for a series of substituted acetylide complexes of platinum.<sup>25</sup> They also noted that the entire class of compounds seems to crystallize in noncentrosymmetric space groups. The two ruthenium complexes (44, 45) would be worth testing because 44 has a delocalized sulfur system connected to an acetylenic group and 45 has a stryryl group  $\sigma$ -bonded to ruthenium. Ruthenium bipyridine complexes are known to show very weak SHG.<sup>26</sup>

The triscinnamylidene copper complexes (46, 47) are intriguing materials because copper coordination can orient the cinnamylidene groups. In the case of the trifluoromethanesulfonate complex (46), trigonal planar geometry results in the cinnamylidene groups lining up parallel and in the same direction.<sup>27</sup> Copper could promote SHG by orienting the  $\pi$ -conjugated groups.

## CONCLUSION

Our initial tests show that on-line databases offer ample promise as tools for screening materials, but the tools are far from perfect. The paucity of data and gaps in coverage are serious drawbacks. While we are optimistic that coverage gaps will be closed, the shortage of data is a more serious problem. In general, an empirical approach where one takes materials known to have the sought-after bulk property and match them with other materials having similar structures and physical properties is probably not feasible because of the shortage of data. The challenge then is to use theory and chemical intuition to find good indicator properties. A good indicator property would necessarily be one that is known for many materials and can be related to the sought-after bulk property.

The ability to combine structural information with numerical data of many types in searching strategies is a powerful tool. While it is not possible from these early studies to derive algorithms for choosing candidates for SHG, the systematic method for searching yields some promising insights. Several classes of candidates came to light because of the method. For example, the cyclic phosphoric nitrides, the polar  $\sigma$ -bonded cyclopentadienyl complexes of hafnium and zirconium, and copper azadienes are unexpected candidate materials.

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## REFERENCES AND NOTES

- Lehn, J. M. Optical Properties and the Intermolecular Bond: By Way of Extension from Molecular to Supramolecular Materials. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chmela, D. S., Zyss, J., Eds.; Academic: New York, 1987; Vol. 2, pp 215-19.
- Brandt, H. E.; Thompson, B. J., Eds. *Selected Papers on Nonlinear Optics*. SPIE Milestone Series, Vol. MS 32; SPIE: Bellingham, Washington, 1991.
- Velsko, S. P. Strategy and Tactics in the Search for New Harmonic-Generating Crystals. In *Materials for Nonlinear Optics*; ACS Symposium Series 455; American Chemical Society: Washington, D.C., 1991; pp 343-59.
- Webb, M. S.; Eimerl, D.; Velsko, S. P. Wavelength Insensitive Phase-Matched Second-harmonic Generation in Partially Deuterated KDP. *J. Opt. Soc. Am. B: Opt. Phys.* **1992**, *9* (7), 1118-27.
- Webb, M. S.; Eimerl, D.; Velsko, S. P. High Bandwidth Second-harmonic Generation in Partially Deuterated KDP. *Proc. SPIE-Int. Soc. Opt. Eng.* **1992**, *1626* (Nonlinear Opt., III), 318-24.
- Norton, M. A.; Eimerl, D.; Ebberts, C. A.; Velsko, S. P.; Petty, C. S. KDP Frequency Doubler for High Average Power Applications. *Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, *1223* (Solid State, Lasers), 75-83.
- Monaco, S. B.; Davis, L. E.; Velsko, S. P.; Wang, F. T.; Eimerl, D.; Zalkin, A. Synthesis and Characterization of Chemical Analogs of L-Arginine Phosphate. *J. Cryst. Growth* **1987**, *85* (1-2), 252-5.
- Hann, R. A.; Bloor, D., Eds. *Organic Materials for Non-Linear Optics*; Special Publication 69; Royal Society of Chemistry: London, 1989.
- Hann, R. A.; Bloor, D., Eds. *Organic Materials for Non-Linear Optics II*; Special Publication 91; Royal Society of Chemistry: London, 1991.
- Williams, D. J., Ed. *Nonlinear Properties of Organic and Polymeric Materials*. ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983.
- Chmela, D. S.; Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic: London, 1987; Vols. 1 and 2.
- Tam, W.; Guerin, B.; Calabrese, J. C.; Stevenson, S. H. 3-Methyl-4-methoxy-4'-nitrostilbene (MMONS): Crystal Structure of a Highly Efficient Material for Second-harmonic Generation. *Chem. Phys. Lett.* **1989**, *154* (2), 93-6.
- Calabrese, J. C.; Tam, W. Organometallics for Nonlinear Optics: Metal-pyridine and Bipyridine Complexes. *Chem. Phys. Lett.* **1987**, *133* (3), 244-5.
- Bandy, J. A.; Bunting, H. E.; Green, M. L. H.; Marder, S. R.; Thompson, M. E.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. The Synthesis of Ferrocenyl Compounds with Second-order Optical Nonlinearities. In *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; Special Publication 69; Royal Society of Chemistry: London, 1989, 219-24.
- Cheng, L. T.; Tam, W.; Meredith, G. R. Quadratic Hyperpolarizabilities of Some Organometallic Compounds. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 137-53.
- Kanis, D. R.; Ratner, M. A.; Marks, T. J. Calculation and Electronic Description of Quadratic Hyperpolarizabilities toward a molecular Understanding of NLO Responses in Organotransition Metal Chromophores. *J. Am. Chem. Soc.* **1992**, *114*, 10338.
- Frazier, C. C.; Harvey, M. A.; Cockerham, M. P.; Hand, H. M.; Chauchard, E. A.; Lee, C. H. Second-harmonic Generation in Transition-Metal-Organic Compounds. *J. Phys. Chem.* **1986**, *90* 5703-6.
- Rosca, S.; Nentzescu, C. D. Resolution of Enantiomeric Amino-derivatives of Arene-tricarbonyl-chromium(0). *Rev. Roum. Chim.* **1970**, *15*, 259-63.
- Kulishov, V. I.; Brainina, E. M.; Boki, N. G.; Struchkov, Y. T. X-Ray Structure of Tetracyclopentadienylhafnium. *J. Organomet. Chem.* **1972**, *36*, 333-4.
- Kulishov, V. I.; Brainina, E. M.; Boki, N. G.; Struchkov, Y. T. Crystal and Molecular Structure of Tetracyclopentadienylzirconium. *Chem. Commun.* **1970**, 475.
- Schluter, A. W.; Jacobson, R. A. Crystal Structure of Pentameric Phosphorus Nitride Dichloride. *J. Chem. Soc. A* **1968**, No. 19, 2317-25.
- Lund, L. G.; Paddock, N. L.; Proctor, J. E.; Searle, H. T. Phosphonitrilic Derivatives. Part I. The Preparation Cyclic and Linear Phosphonitrilic Chlorides. *J. Chem. Soc.* **1960**, 2542-7.
- Branton, G. R.; Brion, C. E.; Frost, D. C. K. A. R.; Paddock, N. L. Phosphonitrilic derivatives. XVIII. Ionization Potentials, Orbital Symmetry, and  $\pi$ -Electron Interactions. *J. Chem. Soc. A* **1970**, No. 1, 151-6.
- Chow, P.; Zargarian, D.; Taylor, N. J.; Marder, T. B. Synthesis of hydridobis(acetylide) complexes of rhodium and the molecular structures of mer-trans-[Rh(PMe<sub>3</sub>)<sub>3</sub>(H)(C.tplbond.CPh)<sub>2</sub>] and mer-trans-[Rh(dmpe)(H)(C.tplbond.CSiMe<sub>3</sub>)<sub>2</sub>](mu.-dmpe)] (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PM<sub>2</sub>). *J. Chem. Soc., Chem. Commun.* **1989**, 1545-7.
- Marder, T. B.; Lesley, G.; Yuan, Z.; Fyfe, H. B.; Chow, P.; Stringer, G.; Jobe, I. R.; Taylor, N. J.; Williams, I. D.; Kurtz, S. K. Transition Metal Acetylides for Nonlinear Optical Properties. *Materials for*

- Nonlinear Optics*; Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, D.C., 1991; pp 605–15.
- (26) Sakaguchi, H.; Nagamura, T.; Matsuo, T. Quadratic Nonlinear Optical Properties of Ruthenium(II)-bipyridine Complexes in Crystalline Powders. *Appl. Organomet. Chem.* **1991**, *5* (4), 257–60.
- (27) Stamp, L.; Dieck, H. T. Copper(I) Complexes with Unsaturated Nitrogen-Ligands. Part IV. Synthesis and Structure of Copper(I) Monoazadiene Complexes. *Inorg. Chim. Acta* **1988**, *147*, 199–206.
- (28) Tam, W.; Calabrese, J. C. Oxidative Addition of Pd(0) and Pt(0) with Aromatic Halides: Material for Second Harmonic Generation. *Chem. Phys. Lett.* **1988**, *144* (1), 79–82.
- (29) Brown, G. M.; Frazier, C. C. The Structure of Tricarbonyl(styrene)-chromium, a Crystal Active in Second-harmonic Generation. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1989**, *C45* (8), 1158–61.
- (30) Lamberth, C.; Murphy, D. M.; Mingos, D. M. P. Second Harmonic Generation Properties of some Coordination Compounds Based on Pentadionate and Polyene Ligands. In *Organic Materials for Nonlinear Optics*; Hann, R. A., Bloor, D., Eds.; Special Publication 91; Royal Society of Chemistry: London, 1989; pp 183–9.
- (31) Yamazaki, Y.; Hosono, K.; Matsuda, H.; Minami, N.; Asai, M.; Nakanishi, H. Enzymic Preparation of Organometallic Compounds with Second-order Optical Nonlinearities. *Biotechnol. Bioeng.* **1991**, *38* (10), 1218–22.
- (32) Copley, R. C. B.; Lamberth, C.; Machell, J.; Mingos, D. M. P.; Murphy, D. M.; Powell, H. Second-harmonic Generation Properties of Some Coordination Compounds Based on Pentanedionate Ligands. *J. Mater. Chem.* **1991**, *No. 4*, 583–9.
- (33) Fischer, E. O.; Schreiner, S. Dipole Moments of Aromatic Metal Complexes. *Chem. Ber.* **1959**, *92*, 938–48.
- (34) Buttery, H. J.; Keeling, G.; Kettle, S. F. R.; Paul, I.; Stamper, P. J. Solid-state Studies. Part II. Raman- and Infrared-active Carbonyl Stretching Vibrations of Four Methylbenzenetricarbonylchromium Complexes. *J. Chem. Soc. A* **1969**, *No. 15*, 2224–7.
- (35) Apostolidis, C.; Kanellakopoulos, B.; Maier, R.; Rebizant, J.; Ziegler, M. L. Bis(cyclopentadienyl)technetium(III) und Tris(cyclopentadienyl)-technetium(III), Neue Metallorganische Verbindungen des dreiwertigen Technetiums. *J. Organomet. Chem.* **1990**, *396*, 315–26.
- (36) Strohmeier, W.; Hellman, H. Einfluss des Lösungsmittels und der Liganden auf das Dipolmoment von Aromatenmetalltricarbonylen (Influence of the solvent and of the ligands on the dipole moment of arene metal carbonyls). *Z. Electrochem.* **1963**, *67*, 190–3.
- (37) Kharlamova, E. N.; Brainina, E. M.; Guryanova, E. N. Dipole Moments of Some Cyclopentadienyl Compounds of Zirconium and Hafnium. *Izv. Akad. Nauk SSSR Ser. Khim.* **1970**, 2621–2.
- (38) Chatt, J.; Mann, F. G.; Wells, A. F. The Constitution of Complex Metallic Salts. Part IX, The Oxalate Radical as a Bridging Group between Metallic Atoms. The Structure and Reactions of Dichlorobis(tri-n-butylphosphine)-mew-oxalato-dipalladium. *J. Chem. Soc.* **1938**, 2090.
- (39) Greenfield, H.; Sternberg, H. W.; Friedel, R. A.; Wotiz, J. H.; Markby, R.; Wender, I. Acetylenic Dicobalt Hexacarbonyls. Organometallic Compounds Derived from Alkynes and Dicobalt Octacarbonyl. *J. Am. Chem. Soc.* **1956**, *78*, 120–4.
- (40) Sly, W. G. The Molecular Configuration of Dicobalt Hexacarbonyl Diphenylacetylene. *J. Am. Chem. Soc.* **1959**, *81*, 18–20.
- (41) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. Reactions of Transition-metal Sigma-acetylide Complexes XII. Formal Insertion of CS<sub>2</sub> into the M-C(sp) Bond of Ru(C<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>(eta-C<sub>5</sub>H<sub>5</sub>). X-Ray Crystal Structure of Ru(eta-S<sub>2</sub>CC<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>(eta-C<sub>5</sub>H<sub>5</sub>). *J. Organomet. Chem.* **1988**, *352*, 199–204.
- (42) Torres, M. R. A.; Ros, J. Reactions of Ru(CO)Cl(RCCHR')(PPh<sub>3</sub>)<sub>2</sub> with Carboxylates. The Crystal Structure of Ru(O<sub>2</sub>CMe)(CO)-(HCCPh)(PPh<sub>3</sub>)<sub>2</sub>. *J. Organomet. Chem.* **1990**, *385*, 379–386.
- (43) Fischer, H.; Gerbing, U.; Tiriliomis, A.; Mueller, G. Transition-metal-coordinated Heteroolefins as Synthetic Building Blocks. Thio- and Selenoacrylamides from 1-(diethylamino)-1-propyne and Heteroaldehyde- and Ketone-Complexes. *Chem. Ber.* **1988**, *121*, 2095–102.
- (44) Ito, Y.; Inouye, M.; Mukakami, M.; Shiro, M. The Synthesis and Reaction of N-Phenylalkynylimine-hexacarbonyldicobalt Complexes. *J. Organomet. Chem.* **1990**, *385*, 399–408.
- (45) Buttery, H. J.; Keeling, G.; Kettle, S. F. A.; Paul, I.; Stamper, P. J. Solid-state Studies. Part III. Raman- and Infrared-active Carbonyl Stretching Vibrations of 1,3- and 1,4-Dimethylbenzenetricarbonylchromium. *J. Chem. Soc. A* **1970**, *No. 3*, 471–4.
- (46) *International Tables for Crystallography, Space Group Symmetry*; Hann, T., Ed.; Kluwer, Dordrecht, The Netherlands, 1989; Vol. A.