

# **Lambda-Like Chromophores for Chiral Nonlinear Optical Materials**

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The first hyperpolarizability of several  $\Lambda$ -like chromophores including Malachite Green and Brilliant Green were measured by means of Kleinman-disallowed hyper-Rayleigh (harmonic light) scattering (KD-HRS). Such chromophores are of interest as components of a new class of chiral and axial macroscopic materials. Light scattering measurements were carried out in the both the non-resonant and in the anomalous dispersion regime in order to compare experimental results with a two-level model that indicates that B-symmetry excited states will contribute. Large hyperpolarizabilities were observed in all cases and evidence that the lowest-lying excited state has B symmetry was found in some molecules.

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Second-order nonlinear optical phenomena such as second harmonic generation and the linear electro-optic effect require materials lacking an inversion center. It has long been recognized that chiral media (media that can not be superimposed on their mirror images and thus lack an inversion center) fit this requirement.[1] In an earlier publication we have described our approach to optimizing chiral nonlinear optical media starting from the point of view of molecular materials that are easily fabricated into macroscopic media and material phases that are stable.[2] Materials possessing uniaxial or biaxial symmetry such as nematic, smectic and columnar liquid crystals and axially oriented (stretched) polymers are candidates. For example, liquid crystal phases composed of dipolar molecules are extremely stable and are the staple of the ubiquitous liquid crystal display industry. Thus, like octupolar materials,[3] axially ordered chiral media do not require the high free energy cost usually paid for aligning polar molecules in a polar fashion. The aim of our studies is to exploit the properties of chiral media to form nonpolar bulk nonlinear optical materials regardless of the polarity of the molecular constituents. We note that chiral molecules are not necessary for large chiral nonlinear optical responses; a chiral arrangement of nonchiral molecules is sufficient. Indeed, Van Elshocht et al. have recently demonstrated how chiral helical arrangements of  $\Lambda$ -like molecules can be synthesized and processed so as to exhibit sizable chiral, Kleinman disallowed second order nonlinear optical effects.[4]

As has been previously discussed, the second harmonic hyperpolarizability tensor  $\mathbf{b}_{ijk}$  can be decomposed into four rotationally irreducible tensor parts – a fully symmetric traceless third-rank tensor, a symmetric traceless second-rank tensor and two vectors. The six (scalar) rotational invariant figure of merit are associated with the squares of these tensors and the

(complex) interference between the two vectors.[2] Tensors of lower rank can be embedded into a third-rank tensor form so that an arbitrary tensor  $\mathbf{b}$  can be formally written as

$$\mathbf{b}_{ijk} = \mathbf{b}_{ijk}^{(3s)} + \mathbf{b}_{ijk}^{(2m)} + \mathbf{b}_{ijk}^{(1s)} + \mathbf{b}_{ijk}^{(1m)} \quad (1)$$

where the superscript indicates the tensor rank and the permutation symmetry (s=symmetric, m=mixed).

The two symmetry groups (of the bulk) that describe uniaxial and biaxial chiral media are  $D_\infty$  and  $D_2$ . The former has a single nonpolar axis and can be realized in uniaxially stretched (chiral) polymers or in uniaxial liquid crystal phases (e.g. nematic or smectic  $A$ ). The biaxial  $D_2$  group has three distinct orthogonal two-fold axes. It (or its sub-group  $C_2$ ) occurs in biaxial liquid crystal phases (e.g. smectic  $C$ ) and in liquid-crystal polymers in which the backbone defines one direction and the side chain liquid crystal moieties defining the other. In the uniaxial group  $D_\infty$ , the second-rank tensor is the only nonzero irreducible component of  $\mathbf{c}^{(2)}$  and the Kleinman non-symmetric  $\mathbf{b}_{ijk}^{(2m)}$  is the sole contribution. Since this is a Kleinman non-symmetric component, only molecules possessing multidimensional charge transfer, that is molecules in which the transition dipole moment is not parallel to the dipole moment difference between excited and ground states, will exhibit this response.[5] The hyperpolarizability of a  $D_2$  material comprises both possible nonpolar irreducible components of second and third rank. These second and third rank molecular tensors will contribute according to their orientational distribution within the bulk material and a preferred orientation can be achieved easily by steric packing. The details of chiral macroscopic arrangement and its optimization are discussed elsewhere. [6]

In order to optimize the second-rank tensor component, we have examined the quantum-mechanical perturbation theory that provides a compact expression for  $\mathbf{b}$  as an infinite sum over the energy states of the chromophore.[2] The sum can normally be truncated since only a few

quantum states will contribute. It has been generally shown that the states that optimize Kleinman-disallowed components of  $\mathbf{b}$  would have  $\mathbf{m}_{gn}$ , the transition dipole moment between ground and excited states, perpendicular to  $\Delta\bar{\mathbf{m}}_{ng} = \bar{\mathbf{m}}_{nn} - \bar{\mathbf{m}}_{gg}$ , the change in the molecular dipole moment. We consider here the special case of a single excited state (two-level approximation) for which the second-rank component of  $\mathbf{b}$  can be written as

$$\mathbf{b}_{(2m)}^{ij} = \frac{3w^2}{\hbar^2 (w_{ng}^2 - w^2)(w_{ng}^2 - 4w^2)} \left\{ [\bar{\mathbf{m}}_{ng} \times \Delta\bar{\mathbf{m}}_{ng}]^i \mathbf{m}_{ng}^j + [\bar{\mathbf{m}}_{ng} \times \Delta\bar{\mathbf{m}}_{ng}]^j \mathbf{m}_{ng}^i \right\} \quad (2)$$

Even though the standard two-level model is not adequate for the description of the molecular response of two- and three-dimensional molecules, our analysis suggests that the hyperpolarizability components of interest to us in  $\Lambda$ -like (or quasi- $\Lambda$ -like) molecules consisting of two donors on the “legs” of a conjugated lambda shape and an acceptor at the apex (or vice versa) can be described by Eq. (2) in many cases, provided that the states with the correct symmetries (which are not necessarily the lowest lying excited states) are included in the sum.[2] For understanding the low-lying electronic states,  $\Lambda$ -like molecules that have a single conjugated region consisting of an apex and two identical “feet” can be treated as having  $C_{2v}$  or  $C_2$  symmetry. The electronic states of these molecules can be either symmetric (A-type) or antisymmetric (B-type) functions with respect to the  $180^\circ$  rotation about the symmetry axis. This results in two distinct possibilities for the transition dipole moment: it must be either parallel (for an A state) or perpendicular (for a B state) to the molecular rotation axis, which corresponds to its dipole. Thus, according to Eq. (2), only B-states will contribute to  $\mathbf{b}_{ijk}^{(2)}$  and, in fact, have optimal geometry since the B-state transition moment is orthogonal to the symmetry axis [2,5]. To maximize the nonlinear optical response in chiral media composed of  $\Lambda$ -like molecules, the lowest-lying state should have substantial B-character. Semiempirical calculations for several  $\Lambda$ -

like molecules indicate that some molecules of this type indeed do have quite strongly absorbing low-lying states with the appropriate symmetry [7]. In addition, Eq. (2) indicates that the molecular response will be enhanced in the anomalous dispersion regime, e.g. for second harmonic generation when the fundamental laser frequency is lower energy but the second harmonic is higher in energy than the energy of the relevant (B type) quantum state. In contradistinction the (two level) contributions of a single quantum state (whether A or B type) to the Kleinman allowed vector or octupolar hyperpolarizabilities decreases in the anomalous dispersion regime.

Efficient nonlinear optical response in  $C_2$  or similar chromophores with large Kleinman disallowed hyperpolarizabilities requires a low-lying B-state with large charge transfer in this state as would be seen in chromophores with strong donors and acceptors. In linear molecules, this charge transfer is necessarily parallel to the long axis of the molecule. However, if two such chromophores are connected so as to make a  $\Lambda$ -like molecule, then it is expected that, of the two lowest-lying excited states, one will have A-type symmetry and the other of which will have B-type symmetry. Whether an A or B type state will be the lowest-lying state is a more complicated issue. For practical considerations in nonlinear optical devices operating in the visible, it is most desirable to have the B-state as the lowest lying excited state.[2] We describe indicative AM1 quantum chemical calculations briefly below. However, either more complicated quantum chemistry calculations or appropriate measurements can give more definitive results.

We also note that the states of differing symmetry contribute to different sum rules, so that the oscillator strength of each can be independently optimized. The symmetry analysis described here provides for necessary, but not sufficient conditions for large Kleinman-

disallowed nonlinear optical response. Detailed theoretical and experimental studies are needed in order to determine the factors leading to large dipole transitions that would be sufficient for producing large responses.

In this letter we further explore the potential for application of  $\Lambda$ -like molecules in axial and chiral nonlinear optical materials. We present measurements of rotational invariants of the first hyperpolarizability tensor  $\mathbf{b}$  for several  $\Lambda$ -like multidimensional molecules at several excitation wavelengths in near infrared performed by means of the Kleinman-disallowed Hyper Rayleigh scattering (KD-HRS) technique we have previously reported [8, 9]. The analysis of the second-rank component of  $\mathbf{b}$ , whose presence is essential in nonpolar nonlinear optical systems described above, is emphasized. We intend to demonstrate that Eq. (2) correctly suggests that such these molecules can have substantial  $\mathbf{b}_{ijk}^{(2)}$  response, and we will examine the nature of the states by measurements inside and outside of the anomalous dispersion regime. Measurements are performed on “model” compounds with the intention of verifying some of the concepts and theories related to nonpolar chiral nonlinear optical response. We do not expect these particular compounds to be the basis of a new technology, but rather to provide a conceptual basis for improved materials to be developed in future work.

The molecular structures of the materials studied here are shown in Figure 1. Crystal Violet (CV), Malachite Green (MG) and Brilliant Green (BG) are well-known triarylmethane dyes and the samples studied were obtained from *Aldrich*. MG was used in form of the carbinol hydrochloride (dye content ~85%) which dehydrates rapidly to give the chloride salt of the dye upon dissolution. The CV and BG dyes are chloride and hydrogen sulfate salts, respectively, both with dye content of ~95%. Crystal Violet is often considered to have a naïve three-fold symmetry. However, our measurements showed a rather strong contribution of vector

components that are not allowed in non-polar point groups such as  $D_3$  or  $D_{3h}$ , and this evidence suggests deviation from these symmetries in the ground state in this solvent. These results confirm other studies that suggest that CV is less symmetric than expected.[10, 11] Unlike Crystal Violet, Malachite Green and Brilliant Green have only two out of three phenyl rings substituted with amine donors so that the resulting symmetry would be expected to be  $C_{2v}$  or, given the steric repulsions amongst the rings,  $C_2$ . Experimental results indicating deviation of Brilliant Green from Kleinman symmetry have been previously reported [12]. The two molecules synthesized for this study (Compounds RT9090 and 1955-49) are  $\Lambda$ -shaped chromophores with the acceptor in the middle and donors on the legs of  $\Lambda$ . The RT9090 dye was synthesized by a standard Knoevenagel condensation between the pair of activated *m*-xylene and aromatic aldehyde.[13] and the 1955-49 dye was prepared by taking advantage of the reaction between an organolithium reagent and a nitrile followed by reaction of the metallated imine with excess malononitrile.[14] These molecules are conventional linear and dipolar NLO chromophores except that they share a common central acceptor group that results in a  $\Lambda$  geometry of the overall molecule. The UV-Vis absorption spectra of the studied  $\Lambda$ -like chromophores are shown in Fig. 2. All the materials show a main absorption peak with apparent multiple structure in the visible range as well as a much weaker secondary peak in the violet-near UV region.

The KD-HRS technique for determining the complete set of rotation invariants of the first hyperpolarizability tensor in Kleinman-disallowed regime was described in detail in Reference [9]. Briefly, the light from an optical parametric oscillator tunable through the near infrared is sent through a polarizer and a quarter-wave plate creating an arbitrary elliptical polarization and focused into a triangular quartz cell containing the chromophore in a filtered acetone solution.

The choice of solvents was discussed previously.[8] The scattered second harmonic light is collected at a  $45^\circ$  angle and focused on a photomultiplier tube after a single elliptical polarization from the entire signal is selected with a similar system of a quarter-wave plate and a polarizer. The  $45^\circ$ -scattering angle is superior to the conventional  $90^\circ$ -scattering angle experiment as the former provides, with a proper choice of input and output polarizations, information sufficient to determine all six possible rotational invariants of  $\mathbf{b}$  while the latter reveals only certain linear combinations of the six scalars.

In our experiment, the intensity of a well-defined (elliptical) polarization of the outgoing second harmonic light is recorded as a function of the polarization of the fundamental frequency light. The values of the rotational invariants of  $\mathbf{b}$  are extracted from the signal by means of least-square fitting. Since most of our measurement wavelengths lie in the vicinity of molecular resonances, two-photon fluorescence may be a competing process that can complicate the measurements of  $\mathbf{b}$ . To assure the dominance of the second harmonic signal over two-photon fluorescence, we measured the spectral content of the scattered light for all the chromophores at the laser excitation wavelengths used in this study. The measurements showed that the level of the second harmonic signal is comfortably above the signal from multiphoton fluorescence within tens of nanometers from the SH wavelength. The scattering at more remote wavelengths was blocked with a narrow band-pass interference filter for every SH wavelength used.

Table 1 summarizes the results of our measurements at the excitation wavelengths of 1560, 1340, 1064 and 780 nm. The figures of merit of the two vector ( $I_{ss}$  and  $I_{mm}$ ), the second rank ( $Q_{mm}$ ) and the third rank ( $\beta_{ss}$ ) components are defined as square roots of their scalar rotational invariants (see Ref. [9] for precise definitions). Absolute values of invariants were found through an external referencing scheme by comparing concentration dependencies of the

harmonic light intensities of the unknown and reference chromophore. Due to high absorbance of studied chromophores at some second harmonic wavelengths, absorption corrections were included in the fitting function for the concentration dependence. *Para*-nitroaniline (*p*NA) was used as a reference substance at all studied wavelengths. The value of the Kleinman-allowed vector component of *p*NA was derived from an EFISHG measurement at the longest wavelength ( $\mathbf{b}_{EFISH}^{pNA} = 12 \cdot 10^{-30} \text{ esu}$  at 1580 nm taken from Ref. 114 of [15]) and scaled for the other wavelengths accordingly to two-level dispersion model [16]. The vanishingly small Kleinman disallowed response in *p*-NA is confirmation of the need for two-dimensional charge transfer.[9] One notices that all  $\Lambda$ -like molecules studied here possess sizable second rank tensor components ( $\mathbf{b}_{2mm}$ ) and even in the relatively off-resonance, ordinary dispersion regime at 1560 nm excitation, the values are comparable to the Kleinman symmetric ones.

By comparing the values of the ratio  $\mathbf{b}^{(2m)} / \mathbf{b}^{(1s)}$  in the ordinary dispersion regime (for long wavelengths) and the anomalous dispersion regime (1064 nm for Crystal Violet, and 780 nm for all dyes), it is seen that this ratio is substantially larger in the anomalous dispersion regime for BG and MG, but not the other molecules. This, together with the discussion following Eq. (2) suggests that the low lying state or states responsible for the low lying absorption peak in BG and MG has B-character, while this state in the other molecules has A-character. Except in the case of CV (which has unknown symmetry) we have confirmed that these symmetries for the lowest lying excited states would also be predicted by the nature of HOMO and LUMO (highest occupied and lowest unoccupied molecular orbitals) within AM1 quantum chemistry calculations. A more complete dispersion curve along with more precise quantum chemical calculations will establish this more firmly and work along these lines is in progress.

The last two columns of the Table 1 present the depolarization ratios measured in a traditional  $90^\circ$  experiment together with the values that are calculated on the basis of the rotational invariants obtained from a  $45^\circ$  measurement. The depolarization ratio is defined as the ratio of the intensities of the scattered harmonic light polarized perpendicular and parallel to the polarization direction of the fundamental-frequency light  $D = I_{\perp}/I_{\parallel}$  (depending on convention, the definition can be inverted to  $I_{\parallel}/I_{\perp}$ ; the ratios involving intensities of circular polarized light can be also defined).[17] The measured and predicted ratios match remarkably well, which strongly supports the reliability of our results. Note that the depolarization ratio for CV at 1560 nm (both measured and calculated) is rather close to  $2/3$  – the limiting value for a purely octupolar molecule that is derived for a Kleinman symmetric **b**. Obviously, in the generalized theory of Kleinman disallowed hyperpolarizability, such a value can be achieved with various combinations of rotational invariants, and the depolarization ratio alone may become a misleading indication of the character of the chromophore if one does not take into account the Kleinman-disallowed contributions. In the case of MG and BG at 780 nm, the deviation from Kleinman symmetry is apparent even from the depolarization ratio, as it lies far above the values possible in purely Kleinman symmetric case, again supporting evidence for a B-symmetry state.

We have performed measurements of the rotational invariants of the first hyperpolarizability **b** for a series of  $\Lambda$ -like nonlinear chromophores of interest for chiral nonlinear optics. We found that all of the materials examined possess figures of merit (including the Kleinman-disallowed second-rank irreducible component of particular interest here) comparable to their large vector hyperpolarizability. Our results suggest that the lowest excited states of two of the compounds are of the B-character that optimizes this nonlinear optical

response. Further studies will be carried out to rationalize, in detail, the different magnitudes of response as they are related to the relevant electronic transitions.

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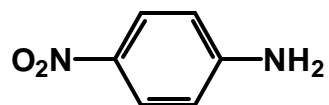


**Table 1** Figures of merit for the irreducible parts of the first hyperpolarizability tensor obtained from 45° KD-HRS experiment. The depolarization ratio is determined from a separate 90° scattering experiment and calculations from the rotational invariants. The shaded areas in the table indicate measurements in the anomalous dispersion regime.

Material		$  \beta_{1ss}  $	$  \beta_{1mm}  $	$  \beta_{2mm}  $	$  \beta_{3ss}  $	Depolarization Ratio			
		(esu x10 <sup>-30</sup> )				90° Experiment		Calc. from 45°	
pNA (reference)	1560 nm	7.12 ±0.16	0.0 ±2.1	3.0 ±2.6	4.95 ±0.23	0.2 ±0.01	0.24 ±0.05		
CV		83.5 ±2.1	72.2 ±2.1	84.1 ±6.5	76.0 ±4.2	0.63 ±0.01	0.65 ±0.06		
MG		69.8 ±1.8	14 ±30	38.6 ±9.5	54.0 ±5.0	0.28 ±0.02	0.28 ±0.10		
BG		92.7 ±2.1	24 ±24	57.6 ±6.1	68.0 ±3.2	0.31 ±0.02	0.30 ±0.04		
pNA (reference)	1340 nm	8.09 ±0.09	0.0 ±2.4	3.6 ±1.1	5.40 ±0.19	0.22 ±0.01	0.23 ±0.06		
RT9090		266.8 ±5.5	15 ±41	128.8 ±4.9	201.4 ±4.6	0.27 ±0.01	0.26 ±0.01		
1955-49		316.0 ±9.4	0 ±98	180 ±35	215 ±11	0.303 ±0.005	0.30 ±0.06		
pNA (reference)	1064	11.2 ±1.6	4.6 ±1.2	2.1 ±2.6	8.2 ±1.2	0.22 ±0.030	0.30 ±0.06		
CV		305 ±58	341 ±72	276 ±52	398 ±81	0.65 ±0.02	0.67 ±0.08		
pNA (reference)	780 nm	56.4 ±5.9	2 ±18	23.4 ±3.8	38.3 ±4.1		0.24 ±0.05		
CV		552 ±42	353 ±34	309 ±36	287 ±31	0.74 ±0.02	0.72 ±0.04		
MG		122 ±10	162 ±18	120 ±13	131 ±14	1.27 ±0.03	1.45 ±0.11		
BG		142 ±11	186 ±16	136 ±12	153 ±13	1.40 ±0.05	1.43 ±0.03		
RT9090		278 ±21	112 ±27	135 ±19	198 ±16	0.39 ±0.01	0.40 ±0.04		
1955-49		289 ±22	119 ±25	167 ±16	200 ±16	0.46 ±0.01	0.46 ±0.04		

**Figure 1.** Molecular structures of studied materials (with  $\lambda_{\max}$  for each material in acetone solution).

**pNA (366nm)**



**CV:**  $\text{R}_1 = \text{N}(\text{CH}_3)_2$

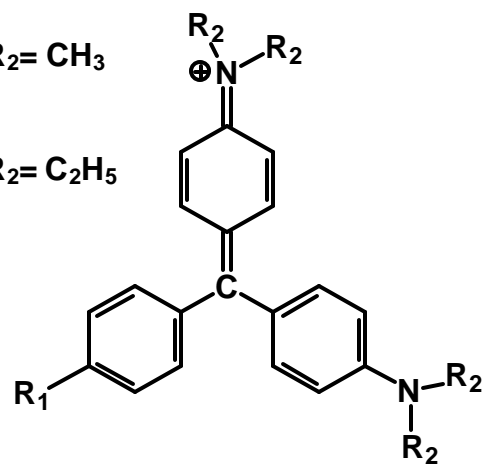
**(588nm)**  $\text{R}_2 = \text{CH}_3$

**MG:**  $\text{R}_1 = \text{H}$

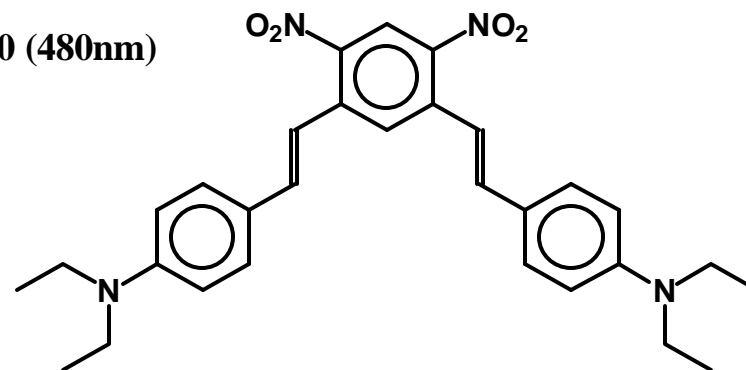
**(615nm)**  $\text{R}_2 = \text{CH}_3$

**BG:**  $\text{R}_1 = \text{H}$

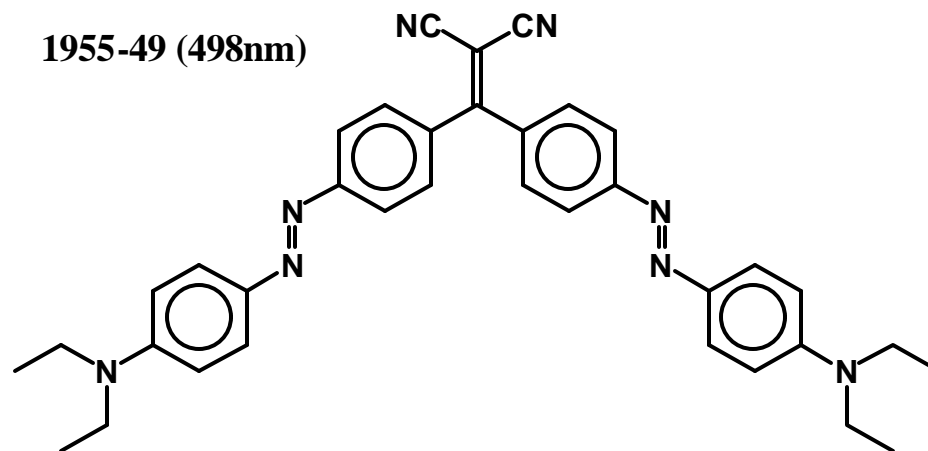
**(625nm)**  $\text{R}_2 = \text{C}_2\text{H}_5$



**RT9090 (480nm)**



**1955-49 (498nm)**



**Figure 2.** Normalized absorption of the studied  $\Lambda$ -like chromophores dissolved in acetone.

