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Molecular First Hyperpolarizability Data for Lanthanate Complexes Containing the Hemicyanine Chromophore

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The molecular nonlinear optical polarizability, or first hyperpolarizability β, of four lanthanate complexes containing the hemicyanine 1-hexadecyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium chromophore has been determined with high precision. The experimental measurement of the phase shift and the demodulation between immediate hyper-Rayleigh scattering and time-delayed multiphoton fluorescence as a function of modulation frequency allows for the simultaneous data analysis of phase and demodulation toward precise values for fluorescence-free hyperpolarizability, multiphoton fluorescence contribution, and fluorescence lifetime. One order of magnitude improvement in precision is obtained with respect to the earlier analysis of demodulation data *only*. This level of precision has been used to show the relative impact of f-orbital filling and ligands on the molecular second-order nonlinear optical response of lanthanate complexes containing a hemicyanine chromophore. Implications for the earlier conclusions about better film formation for lanthanate complexes are discussed.

Introduction

For second-order effects to be observed, noncentrosymmetric arrangements should be achieved. Centrosymmetry precludes all even-order effects, at the macroscopic level of the bulk arrangement of molecules, as well as at the microscopic level of the molecular structure. Hence, for any second-order nonlinear optical (NLO) effect, e.g., frequency doubling of laser light from the near-infrared to the visible blue for larger optical data storage capacity, or electrooptic modulation for increased data transfer bandwidth, a noncentrosymmetric arrangement of noncentrosymmetric molecules is required.[1]

At the molecular level, asymmetrically substituted conjugated π-systems, the so-called acceptor–π–donor (A–π–D) systems, are the preferred molecular templates. Variation in electron-accepting or -donating strength can be correlated with redox potentials.[2,3] The length of the conjugated π-system, by itself symmetric, also determines the linear optical properties, i.e., the refractive index and the extinction coefficient (or the real and imaginary part of the complex refractive index). The structure of the π-system has also an influence through the degree of aromatic or quinoid character of the ground or excited state. The molecular second-order nonlinear optical polarizability, or the first hyperpolarizability β, can be determined indirectly by electric-field-induced second-harmonic generation for dipolar molecules, or directly by hyper-Rayleigh scattering (HRS).[4,5]

At the macroscopic level, for a nonlinear optical susceptibility to be observed, the molecular noncentrosymmetry should be preserved over the physical dimension of the bulk structure.

Noncentrosymmetric crystal growth is not favored by dipolar interaction. A centrosymmetric arrangement of the dipoles lowers the interaction energy. This can be avoided by taking advantage of the hydrophilic–hydrophobic interactions in amphiphilic molecules. These interactions can result in noncentrosymmetric Langmuir–Blodgett (LB) films of nonlinear optical amphiphiles. However, also in these LB films, the intramolecular forces should be controlled in a way to result in a stable noncentrosymmetric structure. Apart from the molecular first hyperpolarizability β, such parameters as number density, order parameter, tilt angle, distribution of tilt angle, and local effective electric field all have an influence on the resulting nonlinear optical susceptibility $\chi^{(2)}$ of the LB film.

It had been found that the use of different lanthanate complexes as the counteranion of a hemicyanine dye (as the noncentrosymmetric amphiphilic NLO chromophore with first hyperpolarizability β) results in improved LB film structures with larger second-order nonlinear optical susceptibilities $\chi^{(2)}$. This had been rationalized in terms of a spacer effect to provide for an ordered separation to avoid inferior (centrosymmetric) J-aggregation, without the danger of phase separation.[6–9] Lanthanate complexes of the 1-methyl-4-{2-[4-(dihexadecyl-amino)phenyl]azo}pyridinium tetrakis(dibenzoylmethanato)-lanthanides(III) (La, Nd, Dy, and Yb) had been incorporated in Langmuir–Blodgett films and had been studied for their film NLO properties. The influence of order parameter, (distribution of) tilt angle, local field, and actual number density complicate the data reduction toward a molecular first hyperpolarizability β. No differences between the values for the first hyperpolarizability had been found, within experimental error, and no comparison with the hemicyanine without lanthanate complexes was made.[6] The experimental values found from coherent second-harmonic generation at 1064 nm ((1.2–3.0) × 10^{-27} esu) are strongly resonantly enhanced, due to the maximum

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absorption at 550 nm for the charge-transfer transition in an LB film (very close to the second-harmonic wavelength of 532 nm). Also the complexes 1-hexadecyl-4-{2-[(4-diethylamino)-phenyl]ethenyl}pyridinium tetrakis(α-thenoyltrifluoroacetonato)-lanthanide(III) (again La, Nd, Dy, and Yb) had been investigated in the LB format for their second-order nonlinear optical susceptibility. Again, no significant difference in deduced molecular first hyperpolarizability for the lanthanate complexes could be inferred.[7] An increase in hyperpolarizability with respect to the hemicyanine bromide of a factor of 3, however, was observed. This was explained as resulting from both the detrimental effect of molecular aggregation in the bromide LB film and the positive effect of charge separation when the bulky lanthanate complexes were used. Both explanations are in terms of molecular interactions in the film. A value for the molecular hyperpolarizability value should not be deduced from these measurements. In another study of Dy complexes with 1-methyl-4-{2-[4-(diethylamino)phenyl]azo}pyridinium as the NLO chromophore, a difference in film susceptibility had been interpreted in terms of different film parameters (length of hydrophobic alkyl chain on a ligand, acting as spacer to improve the segregation of the cations), but has nevertheless been translated to a difference in molecular first hyperpolarizability. Again, no comparison with the hemicyanine without lanthanate complexes was made.[8] Finally, a study of 1-alkyl-4-{2-[4-(dimethylamino)-phenyl]ethenyl}pyridinium lead to the same conclusions: a large enhancement in molecular hyperpolarizability for the hemicyanine with the lanthanate complexes as counteranion with respect to the chromophore with halogenide counteranions, and practically no effect of the nature of the lanthanide rare earth.[9]

It is clear that a difference in film formation can lead to different number density, order parameters, tilt angle, distribution of tilt angle, and local effective field, all parameters that result in a different value for the nonlinear film susceptibility $\chi^{(2)}$, although the molecular first hyperpolarizability β can be the same. The reverse conclusion that the molecular hyperpolarizability is influenced by the film-forming properties is not valid. We have now independently determined the molecular hyperpolarizability for the complexes in solution. From the comparison of these values with the ones determined from the film susceptibility, it is now possible to derive valid conclusions about the film-forming properties for these lanthanate complexes.

Experimental Section

Materials. The complexes used in the present study are shown in Figure 1. The NLO hemicyanine chromophore is the 1-hexadecyl-4-{2-[4-(dimethylamino)phenyl]ethenyl}pyridinium cation in all cases. The ligand is 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPP) (as ligand: 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-onato) or 1,3-diphenyl-1,3-propanedione (or dibenzoylmethane, DBM) (as ligand: 1,3-diphenyl-1,3-propanedionato). The lanthanide(III) is either La, Gd, or Lu. The synthesis and characterization of these complexes has been described previously.[10,11]

Measurement. The direct experimental determination of the molecular hyperpolarizability is based on hyper-Rayleigh scattering by the individual molecular scatterers in solution. [4] Therefore, there is no effect of the film structure and parameters that describe the film properties on the retrieved value for the molecular hyperpolarizability. Hyper-Rayleigh scattering is an incoherent second-order nonlinear scattering process. The intensity of the light that is scattered at the second-harmonic wavelength is proportional to the first hyperpolarizability
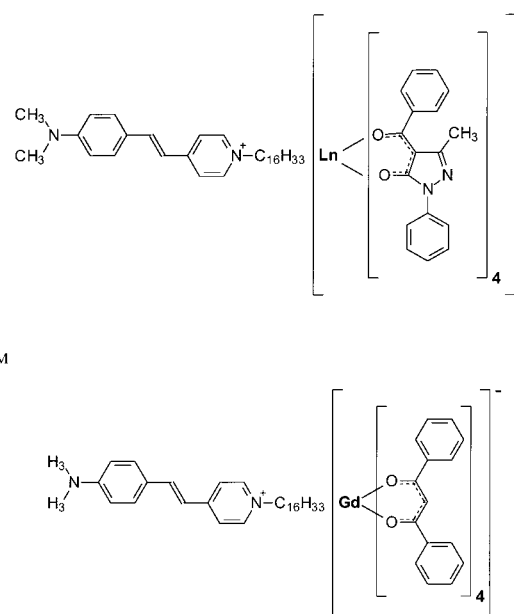

Figure 1. Molecular structure of the lanthanate complexes containing the hemicyanine chromophore used in this study.

squared. The instrumental details of the hyper-Rayleigh scattering experiments have been published previously.[5]

For chromophores that exhibit (multiphoton) fluorescence (MPF), the HRS signal can consist of the nonlinear scattering contribution, but in addition, two- or three-photon fluorescence can also contribute to the signal at the second-harmonic wavelength. This then results in an overestimation of the molecular nonlinearity. Different approaches to deal with the problem of the MPF contribution to the HRS signal have been reported. An MPF-free HRS signal can be obtained by subtracting the broadband MPF background from the sharp HRS peak in the spectral domain.[12,13] We have recently implemented the complete Fourier transform of the most fundamental approach to the problem. This approach is based on the fundamental difference in temporal response between the immediate (hyper-Rayleigh) scattering and the time-delayed (multiphoton) fluorescence in the time domain.[14] In the frequency domain, we measure the demodulation and the phase shift that the fluorescence acquires vs the scattering. The applicability of this approach had been demonstrated with the demodulation *only*.[15-20] The recent addition of the phase data and the simultaneous data reduction of demodulation and phase shift toward the hyperpolarizability, fluorescence contribution, and fluorescence lifetime have resulted in an improvement in precision of 1 order of magnitude.[21] The fundamental wavelength was 1300 nm, obtained from a femtosecond optical parametric oscillator (Spectra-Physics, model OPAL) optically pumped by a titanium:sapphire femtosecond laser (Spectra-Physics, model Tsunami), optically pumped by an argon-ion pump laser (Spectra-Physics, model 2080, with Beamlock option).[17]

Absorption spectra were recorded on a Shimadzu IV-1300 spectrophotometer. The solvent was in all cases chloroform analytical grade.

Results and Discussion

Figure 2 shows the experimental demodulation (○) and phase (□) data as a function of modulation frequency for the Lu(BMPP)$_4^-$ complex counteranion. The solid lines are the fits to a fluorescence-free first hyperpolarizability value, β (the extrapolation of the demodulation curve toward high modulation
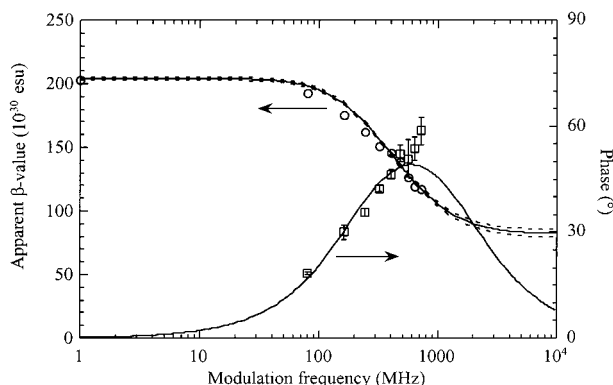
Figure 2. Experimental demodulation ($\bigcirc$) and phase ($\square$) data as a function of modulation frequency for the Lu(BMPP)$_4^-$ complex counteranion. The solid lines are the best fit to a fluorescence-free first hyperpolarizability value, β ($86 \pm 5 \times 10^{-30}$ esu, the extrapolation of the demodulation curve toward high modulation frequencies), a multiphoton fluorescence contribution, X (187 ± 3), and a single fluorescence lifetime, τ (720 ± 20 ps).

TABLE 1: Results from Hyper-Rayleigh Scattering Studies with Fluorescence suppression, Results of Data Analysis Combining Demodulation and Phase Data[a]

	La, $4f^0$, BMPP	Gd, $4f^7$, BMPP	Lu, $4f^{14}$, BMPP	Gd, $4f^7$, DMB	hemicyanine, bromide[b]
λ_{max} (nm)	494	494	494	496	496
β (10^{-30} esu)	87 ± 3	86 ± 3	86 ± 5	54 ± 3	100 ± 6
β_0 (10^{-30} esu)	31 ± 1	31 ± 1	31 ± 1	19 ± 1	36 ± 3
X (10^{-30} esu)	179 ± 3	163 ± 3	187 ± 3	91 ± 2	107
τ (ps)	570 ± 20	640 ± 20	720 ± 20	700 ± 40	670

[a] Fundamental wavelength 1300 nm; solvent chloroform (λ_{max}: wavelength of maximum absorption; β, dynamic first hyperpolarizability; β_0, static first hyperpolarizability; X, multiphoton fluorescence contribution at low frequency; τ, fluorescence lifetime, BMPP, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-onato; DMB, dibenzoylmethane or 1,3-diphenyl-1,3-propanedionato. [b] From ref 19.

frequencies), a multiphoton fluorescence contribution, X, and a single fluorescence lifetime, τ. Table 1 gives the results for the four complexes studied. The actual values for the first hyperpolarizability that were obtained in this study are smaller than the ones obtained for similar lanthanate complexes previously.[6] Apart from the remark that the earlier values for the molecular hyperpolarizability β were indirectly deduced from the film susceptibility $\chi^{(2)}$, which is also a function of number density, order parameter, tilt angle, distribution of tilt angle, and local field factors, the order-of-magnitude difference in value is caused by the difference in resonance enhancement. The wavelength of the second harmonic in the previous study of the same complexes (532 nm) was very close to the wavelength of the maximum absorption in the LB films (490 nm),[9] leading to a large two-photon resonance enhancement factor.

The absorption spectra in chloroform of hemicyanine bromide and the corresponding lanthanate complexes La(BMPP) and Gd(DMB) are shown in Figure 3. All the compounds have an intense charge-transfer band in the visible spectral region. The wavelength of maximum absorption λ_{max} is given in Table 1. A strong solvatochromic effect was observed, in accordance with the observation of second-order nonlinear optical properties for these compounds.[10]

In the present study, the wavelength of the second harmonic (650 nm) is further away from the wavelength of maximum absorption in solution (493 nm), leading to a much smaller enhancement factor. To be able to compare the hyperpolarizability values obtained at different fundamental wavelengths λ_{fund}, the static hyperpolarizability β_0, corrected for the resonance
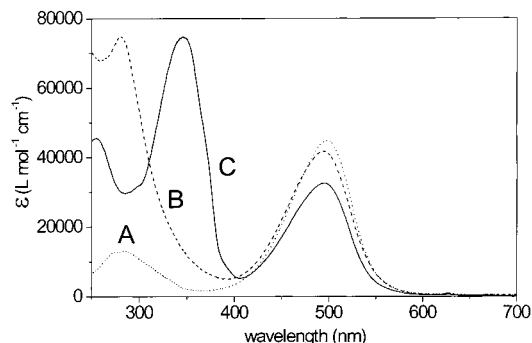

Figure 3. Absorption spectra of hemicyanine bromide (A), La(BMPP)$_4^-$ (B) and Gd(DBM)$_4^-$ (C) in chloroform (concentrated 1.0×10^{-5} M).

enhancement, can be calculated on the basis of the wavelength of maximum absorption λ_{max} for the noncentrosymmetric charge-transfer band and the two-level model:[22]

$$\beta = \beta_0 \frac{\lambda_{max}^{-4}}{(\lambda_{max}^{-2} - \lambda_{fund}^{-2})(\lambda_{max}^{-2} - \lambda_{harm}^{-2})}$$

With this correction factor and the wavelength of maximum absorption λ_{max} from the spectra shown in Figure 3, we arrive at β_0 values for our BMPP complexes of $(31 \pm 1) \times 10^{-30}$ esu, while the previously obtained value for the 4-[4-(dimethylamino)styryl]-1-hexadecylpyridinium iodide from LB films[9] results in a β_0 value ranging from 30×10^{-30} to 45×10^{-30} esu. It is clear, then, that the larger hyperpolarizability values for the complexes with lanthanide counteranions calculated from the film susceptibility are overestimated, due to the positive influence of the better film-forming properties for the latter complexes.

On the other hand, the values found here are in good agreement with hyperpolarizability values for hemicyanine dyes in solution retrieved earlier from hyper-Rayleigh scattering experiments at the same fundamental wavelength (1300 nm). In one study, a dynamic β value of 100×10^{-30} esu was found for the 4-[4-(dimethylamino)styryl]-1-methylpyridinium bromide in chloroform.[19] With the reported value for λ_{max} of 496 nm, a static β_0 value of 36×10^{-30} esu is obtained. In another study, a dynamic β value of 140×10^{-30} esu was found for the 4-[4-(methyloctadecylamino)styryl]-1-methylpyridinium bromide in chloroform.[17] With the value for λ_{max} of 508 nm, a static β_0 value of 45×10^{-30} esu is obtained. This larger value is attributed, through the inductive effect, to the longer alkyl group on the amino nitrogen and the shorter alkyl group on the pyridinium nitrogen.[23] From this comparison, it should be clear that the values for the first hyperpolarizability for the lanthanate complexes are, to first order, determined by the hemicyanine chromophore.

The secondary effect of the nature of the ligand, as observed in LB films,[9] starts already at the molecular level: we see a lower molecular hyperpolarizability β for the DBM ligand with respect to the BMPP ligand. The lower hyperpolarizability cannot be explained through a smaller two-photon resonance enhancement. However, a lower film susceptibility $\chi^{(2)}$ will automatically follow, for the same film-forming properties of the ligand. The reported reduction in film susceptibility $\chi^{(2)}$ upon changing the ligand from BMPP to DBM can then not be taken as indicative of changes in film-forming properties.

To understand the observed effect of the ligand in the counteranion on the molecular hyperpolarizability in solution, it should be realized that the cationic NLO chromophore resides

to a certain extent in the effective local field caused by the counteranion. In a solvent of low polarity, close ion pairs are formed. Chloroform has been shown to induce such close ion pairs.[24] This means that under our experimental conditions, the NLO chromophore did feel the presence of the counteranion. A different counteranion will then indeed result in a different hyperpolarizability, as observed. Although the size of the lanthanide ion itself decreases smoothly over the lanthanide series (the "lanthanide contraction") and, therefore, contraction of the tetrakis(pyrazonolato)lanthanide(III) anion can also be expected, these differences in ion size are too small to have an influence on the first hyperpolarizability. The size of the counteranion is changed much more when the pyrazolone is replaced by the dibenzoylmethane. The smaller hyperpolarizability value for the complex with the smaller DBM ligand can then be explained by the higher charge density on the counteranion. This higher charge density on the anion lowers the charge delocalization in the conjugated hemicyanine cation. This in turn lowers the optical nonlinearity. Off course, Lu(III) has 14 electrons more in its valence shell than La(III). However, the charge densities of La(III) and Lu(III) are very comparable, except for the difference due to the different ionic radius. This is because the 4f valence shell is well shielded from the environment by the full $5s^2 5p^2$ shell.

The observation that the largest value for the first hyperpolarizability is observed for the bromide as counteranion is in contradiction with the charge density being the *only* determining factor. For the charge density to be the *only* factor would require an effective charge delocalization over a large bromide−solvent complex. Although dielectric data for solutions of electrolytes in nonaqueous solvents are very scarce,[25] the high conductivity data for tetraethylammonium halogenides in chloroform[26] seem to indicate that the bromide is not solvated to a large extent. With the unique capability of our experimental setup, it is possible not only to arrive at an MPF-free value for the first hyperpolarizability but also to relate the MPF contribution to the HRS contribution. Comparing this MPF/HRS ratio for the four compounds, we see a constant ratio of approximately 2 for the organic ligands as counteranion. Both HRS and MPF are consequences of a nonlinear polarizability, and both contributions are equivalently reduced for the smaller organic ligand. However, the same MPF/HRS (fluorescence/scattering) ratio drops to 1 for bromide as the counteranion. This is indicative for fluorescence quenching through the heavy-atom effect. Since here the heavy atom is the bromide counteranion, and chloroform is the solvent, close ion pairs are formed, and static quenching should be anticipated, for the fluorophore and quencher are already in contact before excitation. This is exactly what is seen, since the fluorescence lifetime, another parameter that is obtained from our setup, is not systematically varied. On the basis of the observations for these two fluorescence parameters (i.e., the decrease in relative MPF/HRS contribution, yet the constant fluorescence lifetime), we conclude that from the two competing nonlinear processes (i.e., fluorescence and scattering), the fluorescence is statically quenched and, hence, the scattering gains in relative amplitude. This internal static quenching has to be discerned from the external dynamic quenching (shortening of the fluorescence lifetime) that is relied upon by adding a fluorescence quencher to the solution.[27]

The findings about the independence of the molecular second-order nonlinear polarizability from the nature of the lanthanide are in contrast with the dependence of the third-order nonlinear optical response on the nature of the transition metal in phthalocyanines.[28] The observed pattern has been attributed to the filling of the d-orbitals in the transition metals. Third-order, or more general, odd-order effects are not restricted to noncentrosymmetric systems. The more electrons, the larger the odd-order polarizability. Second-order, or more general, even-order effects can only be observed from noncentrosymmetric systems. It is much more the noncentrosymmetric arrangement than the number of electrons that is important for second-order NLO. Therefore, the noncentrosymmetric hemicyanine causes the second-order nonlinear optical response, while different filling of the f-orbitals in the lanthanides does not influence this response. This filling has no influence on the linear optical properties either (same wavelength of maximum absorption).

The effect of the ligand has been explained as an effective local-field effect. It might be hard to substantiate this, since taking the ion pair apart to solvent-separated ion pairs, or even further to fully solvated ion pairs, can only be realized by a more polar solvent. This more polar solvent will by itself also change the local field. Both changing the solvent polarity and separating the ion pair would have an influence on the first hyperpolarizability.

This study of the influence of a strategy to build better noncentrosymmetric films for second-order nonlinear applications on the molecular nonlinearity is very similar to an earlier one. There, however, the strategy of including the hemicyanine dye in an amylose helix resulted not only in good film properties, but also in an increased molecular nonlinearity by a factor of 2.[10] Note that the larger values for β_0 are a consequence of the more polar solvents used. This again can be related to the solvent effect, or to the better dissociation of the ion pairs. If the cationic chromophore is no longer in the local field of the counteranion, the delocalization of the π-electrons in the conjugated chromophore is no longer restricted. The (linear and nonlinear) polarizability is, hence, larger. Apart from this observation, the contrast with the present result is striking: the strategy to enhance the film-forming properties by using lanthanate complexes as counteranions is not effective in improving the molecular nonlinear optical response.

Conclusions

We have experimentally determined the molecular second-order nonlinear optical properties of lanthanate complexes serving as counteranion to a hemicyanine chromophore as the nonlinear moiety. The hyperpolarizability is independent of the nature of the lanthanide but, through the complex anion size, is a function of the size of the ligand on the lanthanide cation. These findings about the molecular nonlinearity are a prerequisite for valid conclusions about better film-forming properties attributed to the lanthanate complexes.

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