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Two-photon absorption with polarization control in chiral compounds

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14. ABSTRACT This report presents the progress made on the project Two-photon absorption with polarization control in chiral compounds in the last period (September 30th/2017 to September 29th/2018). In previous reports we presented some initial results on second and third order nonlinearities in the chiral polymers. In this last period we have been able to conclude the investigation on the Hyper-Rayleigh scattering in the polybinaphthalenes with polarization control. We observed that the first-order hyperpolarizability values for left-circularly polarized light is higher than for right-circularly polarized light, which is in fact related to the polymer symmetry (left-handed). Also, the chirality of the polymer increases significantly the nonlinear response, either by eliminating the dipolar interactions between chromophores, or by the chiral contribution itself. We have also finalized the study of the effect of polarization control on the chiral polymer, which revealed the existence of a hidden two-photon absorption state.					
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Two-photon absorption with polarization control in chiral compounds

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Objectives

The goal of this project is to explore the use of nonlinear spectroscopy with polarization control to obtain additional information, as compared to standard approaches, to investigate the electronic and molecular structure of chiral conjugated polymers.

Status of effort

This report presents the progress made on the project *Two-photon absorption with polarization control in chiral compounds* in the last period (September 30th/2017 to September 29th/2018). In previous reports we presented some initial results on second and third order nonlinearities in the chiral polymers. In this last period we have been able to conclude the investigation on the Hyper-Rayleigh scattering in the polybinaphthalenes with polarization control. We observed that the first-order hyperpolarizability values for left-circularly polarized light is higher than for right-circularly polarized light, which is in fact related to the polymer symmetry (left-handed). Also, the chirality of the polymer increases significantly the nonlinear response, either by eliminating the dipolar interactions between chromophores, or by the chiral contribution itself. We have also finalized the study of the effect of polarization control on the chiral polymer, which revealed the existence of a hidden two-photon absorption state.

Accomplishments

Introduction

The family of chiral conjugated polymers, polybinaphthalenes, has been attracting great deal of attention as they present interesting features for nonlinear optics, particularly the tree-like supramolecular architecture that decreases dipolar interactions [1-3], allowing high chromophore density. Also, chiral donor embedded polybinaphthalenes can benefit from inherent chiral contributions, which can potentially enhance the nonlinear response [2].

The second-order nonlinear optical response of materials, at the molecular level, is related with the first-order hyperpolarizability. For this reason there is great interest to find molecules with high first-order hyperpolarizability. Specifically, polybinaphthalenes are of particular interest for applications in this area as chiral donor-embedded polybinaphthalenes can benefit from contributions inherent to chirality, which can increase the nonlinear response [4-7]. In the first period of this project we have studied the HRS of polybinaphthalenes only for linear polarization. In the last period, we have been able to study the HRS signal for such samples with left- and right-circularly polarized light, evidencing the influence of the chiral structure of the samples on the second order nonlinear process.

Experimental

The four chiral polymers samples were dissolved in THF to concentrations varying from 0.1×10^{-4} mol/l to 0.1×10^{-4} mol/l, which allowed measuring the first hyperpolarizability signal as a function of the concentration. The studied polymers, shown in Fig. 1, were named as POL 1, POL 2, POL 3 and POL 4, according to the chromophore attached to the main polymer chain. The linear absorption spectra of the samples, displayed in Fig. 2, were measured using a Shimadzu UV-1800 spectrophotometer.

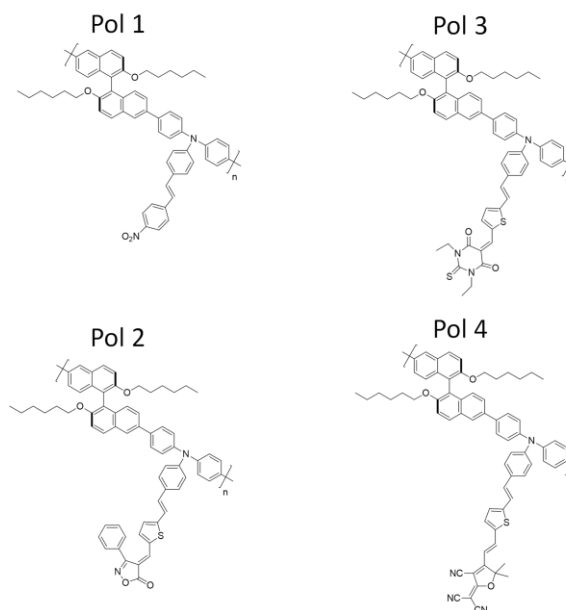


Figure 1 – Repetitive unit structure of the studied polymers.

The first hyperpolarizability was measured using the Hyper-Rayleigh scattering (HRS) method with picosecond pulse trains [8], that allows improving the HRS signal-to-noise ratio. A mode-locked and Q-switched Nd:YAG laser at 1064 nm is used as excitation source.

Such laser delivers 100-ps pulse trains (about 20 pulses) separated by 13 ns. A fast (~ 1 ns rise time) silicon detector (PIN) is used as a reference intensity channel. A quarter-wave plate is used to change polarization from linear to left-circularly and right-circularly. The laser beam is focused into a 1 cm fused silica cuvette containing the sample. The HRS signal is collected perpendicularly to the pump beam direction. To improve the signal-to-noise ratio, a spherical mirror is used to collect part of the signal that is scattered in the opposite direction of the photomultiplier (PMT). Between the sample and the PMT, a telescope is used to achieve a high solid angle. A narrow band pass filter is used to allow only the 532 nm nonlinear scattered signal to be detected by the PMT.

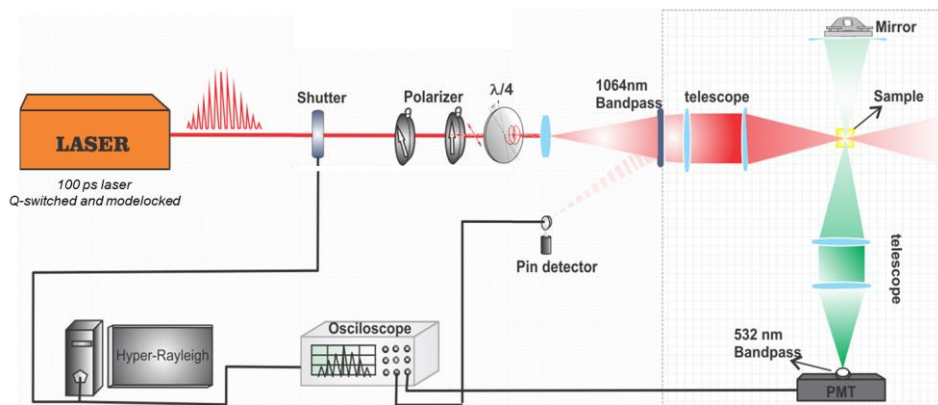


Figure 2 – Hyper-Rayleigh scattering experimental setup.

To investigate the third order optical nonlinearities we have employed the open aperture Z-scan technique [9]. As excitation source we used 120-fs laser pulses from an optical parametric amplifier pumped by 150-fs pulses (775 nm) from a Ti:sapphire chirped pulse amplified system. To control the laser polarization state from linear to circular, we used a broadband zero-order quarter-wave-plate. The wave-plate was placed in a rotating stage, such that we set the angle of rotation of the wave-plate at 0° for linear polarization and at 45° for circular polarization. Also, once the peak and valley position of the Z-scan curves are determined, measurements can be performed by continuously rotating the wave-plate, in order to provide a signal with improved signal/noise ratio. Such system was also described in previous reports.

Results and Discussion

Figure 3 shows the linear absorption spectra of the polymeric samples. As it can be seen, all samples are transparent at 1064nm (ω), wavelength used as excitation in the HRS. However, because samples absorb at 532 nm (2ω) part of the scattered nonlinear signal will be absorbed. Thus, in order to quantify the first-order hyperpolarizability signal properly the obtained signal must be normalized by the linear absorption at 532 nm, which is precisely measured in separated experiments.

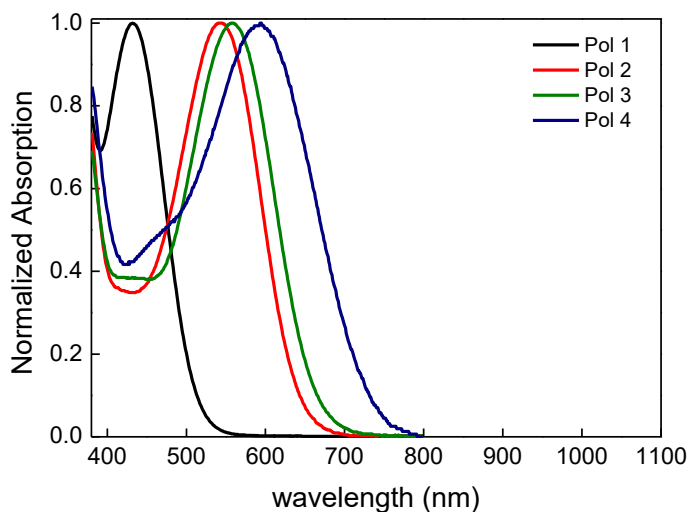


Figure 3 – Normalized absorption of the four chiral polymers dissolved in THF. For wavelengths greater than 800 nm, all polymers are transparent.

In a previous report (1st Interim Report) we have presented the first-order hyperpolarizability for linear polarization. Such results are summarized in Fig. 4. It is interesting to point out that these values are much higher than the one observed for p-nitroaniline (20×10^{-30} cm⁵/esu) [8], a common reference material for such measurements. Also, the first-order hyperpolarizability increases with the asymmetry of the compounds as well as with the push-pull strength. The samples studied here present an increase of the second-order effect if compared with nonchiral polymers [9], which is probably related to the chiral conformation of the polymer [10].

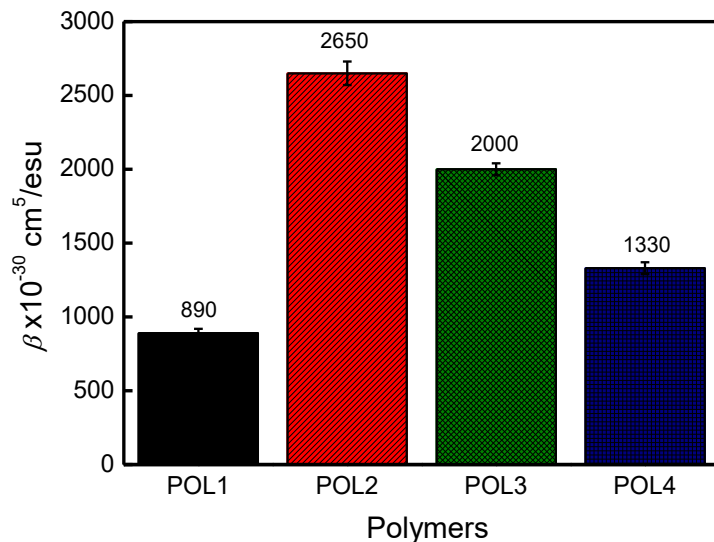


Figure 4 – First-order hyperpolarizability for the samples using linear polarization.

In Fig. 5 it is shown the expected linear behavior of the first-order hyperpolarizability signal ($I(2\omega)/I^2(\omega)$) as a function of the concentration for POL 1, at linear (black), left-circularly (red) and right-circularly (green) polarizations. Such results are compared with the one observed for p-nitroaniline (PNA) (reference sample) for corresponding polarizations, in order to determine the first hyperpolarizability.

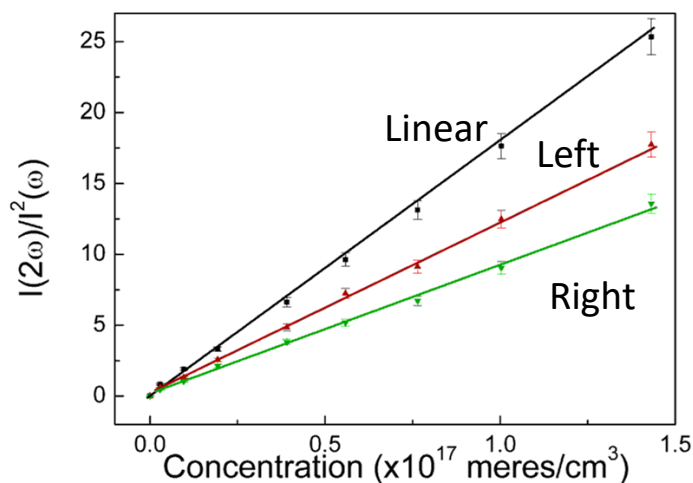


Figure 5 – Linear dependence between the quadratic coefficients for POL 1 at different polarizations. Linear (black), left-circularly (red), right-circularly (green) polarizations.

From results similar to the ones displayed in Fig. 5, for the other polymers, and following the procedures previously described we were able to determine the

first-order hyperpolarizability results, which are displayed in Fig. 6. Such results reveal that β values for left-circularly polarized light is higher than the one for right-circularly polarized light. This can be explained by the fact that all studied polymers are chiral and presents the same symmetry (left-handed). In a simple way, this can be interpreted as if the chirality of the polymer favors or not the generation of the second harmonic, depending on the polarization of the excitation light. It is worth noting that for non-chiral molecules (such as PNA) as well as other molecules already studied in our group such difference, between circular polarizations, have never been observed, thus confirming that the observed effect is related to the polymer chirality.

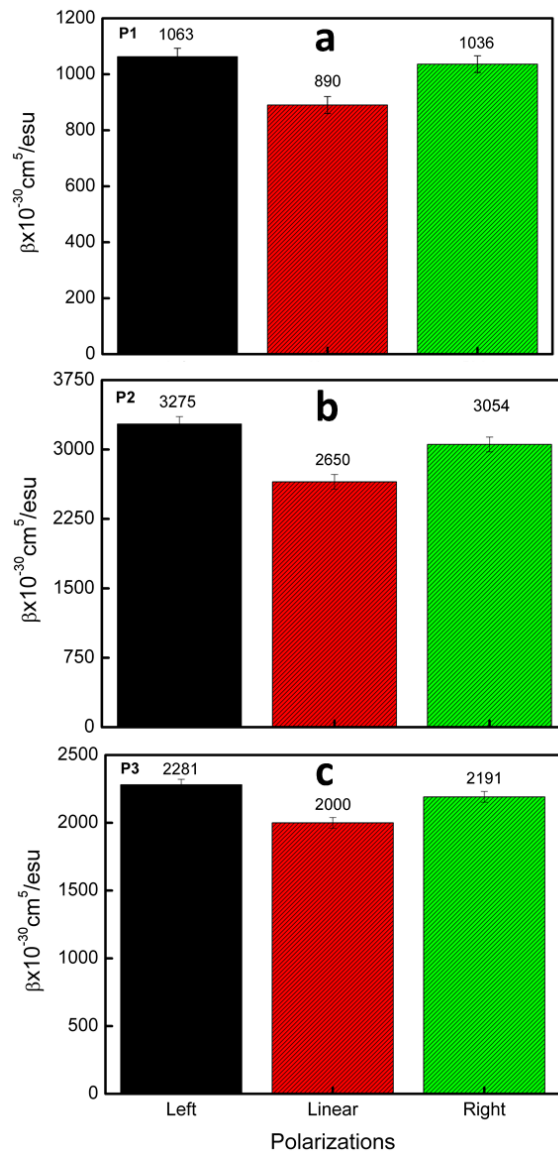


Figure 6 – First-order hyperpolarizability for samples POL 1 (a), POL 2 (b) and POL 3 (c) for linear polarization (red bar), circularly-left (black bar) and circularly-right (green bar).

The high values of β observed for such polymers are related to the chirality of the system that significantly enhances the nonlinear optical response in two ways: (i) by eliminating the dipolar interactions between the chromophores, which allows very high chromophore concentrations, and (ii) by the presence of chiral contributions. Finally, the enhancement effect of the HRS signal due to the electronic transition at the 532 nm region also seems to be an important factor in increasing the nonlinear signal. This can be observed by comparing the values of

the samples POL1 and POL 2, for example. Since the electronic transition is red-shifted for POL 2, the enhancement is higher for such sample. All these factors contribute to the increase of the second order effect of these polymers.

Figure 7 shows the two-photon absorption spectrum for all chiral polymers investigated (open circles – right axes). The corresponding linear absorption spectrum for the samples (dashed line – left axis) is also shown; the band around 340 nm is related to the binaphtalene backbone, while the low energy one is related to the chromophore used in the synthesis [10].

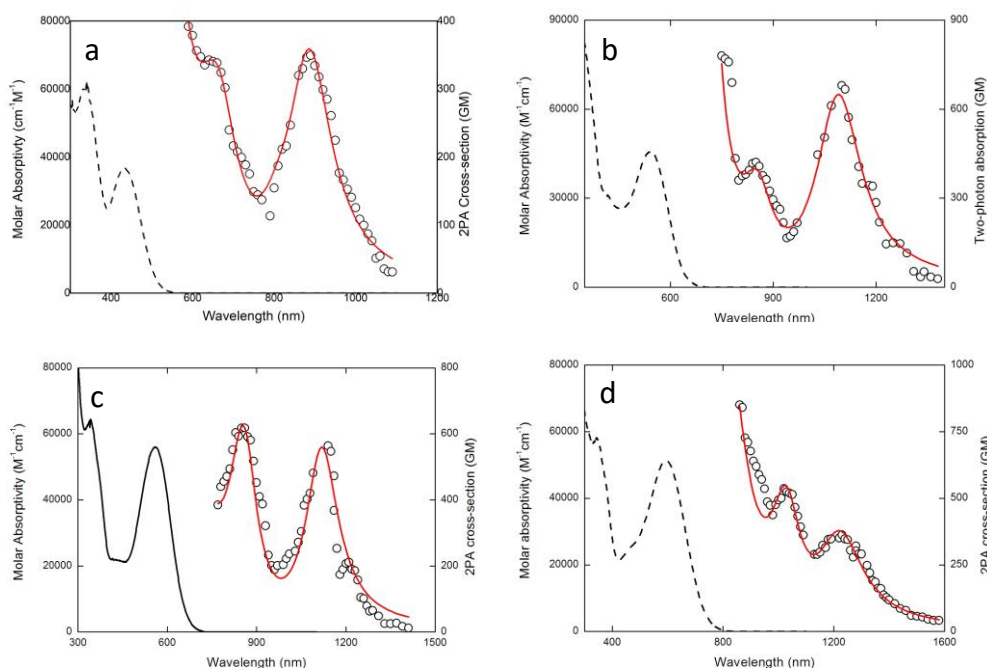


Figure 7: Two-photon absorption cross-section (circles), linear absorption spectrum (black line) and fitting by using a sum-over-states model (red line) for POL 1 (a), POL 2 (b), POL 3 (c) and POL 4 (d).

From the 2PA spectra in Fig. 7 (open circles) it is possible to observe the resonant enhancement effect near the edge of the linear absorption band. For all samples two 2PA bands were observed, which correspond to the energy states observed in the linear absorption band spectrum. Such nonlinear spectrum was modeled using a three level system and the sum-over-states (SOS) approach,

which was fully described in the previous report. As it can be seen in Fig. 7, the fitting (red line) is in very good agreement with the experimental data.

We performed 2PA cross-section measurements at distinct light polarizations (linearly and circularly). To better visualize the behavior of the 2PA process for distinct linear polarization we plot in Fig.

8 the 2PA circular-linear dichroism (defined in Report #1) spectrum for sample POL 1. Such plot shows two regions; one occurs in the range 700-800 nm ($\Omega_{CLD}^{2PA} \cong 0.56$), and the other between 880 nm and 1100 nm ($\Omega_{CLD}^{2PA} \cong 0.45$). This result indicates that there are at least two possible transition states for the sample in its 2PA band, around 800 nm, whose energy separation is approximately 140 meV. Similar behaviors were observed for the other samples.

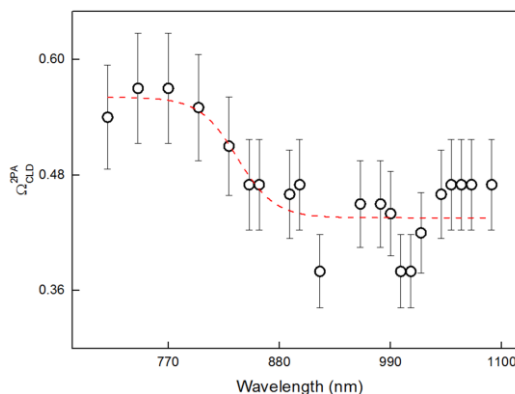


Figure 8: Two-photon absorption circular-linear dichroism (circles) as a function of the studied wavelength for POL 1. The red line is only a visual guide.

We have also measured the nonlinear transmittance for light circularly polarized to the right and to the left. However, we have not been able to observe any difference, considering the experimental errors.

Conclusion

In this period we have concluded the investigation on the first-order hyperpolarizability of four chiral conjugated polymers belonging to the family of polybinaphthalenes, dissolved in THF, for linear, right-circularly and left-circularly polarization. All samples exhibited high second order nonlinearities in comparison with non-chiral conjugated polymers. More interestingly, we observed that the first-order hyperpolarizability for such chiral polymers is higher for left-circular polarization is higher than for right-circular polarization; such results is in agreement with the left-handed chiral symmetry of the studied samples. To the best of our knowledge, this is the first demonstration of such

effect. Furthermore, our results indicate that the polymer chirality increases significantly the nonlinear response due to two factors; avoiding the dipolar interactions between chromophores which allows obtaining a higher chromophore density and by the chiral contribution itself. We have also investigated the two-photon absorption spectrum with polarization control (linear, left- and right-circularly polarizations) will be presented. Different features were observed on the two-photon absorption cross-section for linear and circular polarized lights, from which we were able to determine that two energetically close states are responsible for the observed nonlinear absorption.

Personnel

List of personnel associated with the research:

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New discoveries, inventions, or patent disclosures

None

Publications discoveries, inventions, or patent disclosures in the period of the project

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