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Pyrazoline derivatives with tailored third order nonlinear optical response

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In the present work the third order nonlinear optical response of a series of pyrazoline derivatives has been experimentally investigated. All of the compounds have been prepared as doped poly(methyl methacrylate) thin polymeric films. For the needs of this study the third harmonic generation Maker fringes technique has been employed by using 30 ps laser pulse duration and 1064 nm excitation wavelength. A variety of *push-pull* group of pyrazoline-based derivatives has been studied in order to relate the structural properties with the optical nonlinearity. More specifically, the molecules under investigation have in several cases different electro accepting groups, which are located in various positions of the molecular structure providing two pairs of structural isomers. The experimental results demonstrate a high dependence of the optical nonlinearity due to the functionalization with the different moieties on the pyrazoline derivatives. This fact promotes this class of materials as promising candidates for photonics and optoelectronics applications, where the control of the molecular structure as a mean of tailoring the optical nonlinearities is crucial.

Introduction

Push-pull type molecular systems (i.e. systems that exhibit an electron donating and accepting units) have attracted considerable attention in the past decades, mainly because of the high optical nonlinearities that the exhibit in several cases, due to the delocalized electronic cloud.[1,2] Moreover, as it has been shown in numerous studies, the position and the type of the electron donors and acceptors play an important role in the direction of their nonlinear optical (NLO) response. For this reason, the interest of the scientific community has been focused on the functionalization of the molecular systems which consist of an electron donor and an electron acceptor part, in order to finally tune their NLO properties. In this sense by properly tailoring the molecular structure of a given compound, one can acquire a whole family of molecules that can match several different experimental needs.

Some of the most studied groups of promising organic materials which are expected to exhibit high NLO performance are the compounds based on pyrazole ring. These materials are capable of being used for a broad field of applications. So, pyrazoline derivatives have found great applicability in medicine,[3] but also in many technical domains. They can be used as a source in electroluminescence,[4,5] as the indicators in various pH environment or as optical brighteners due to the Photoinduced-electron transfer.[6] Moreover, based on their useful physicochemical properties they were considered for various applications in photonics, especially in nonlinear optics. It was proven that pyrazoline derivatives can be used as efficient systems for light amplification by stimulated emission or lasing/random lasing action.[7–9] Furthermore, such molecules have high dipole moments or quantum yield and can exhibit efficient fluorescence and Two Photon Absorption.[10–12] They were also investigated in the past for harmonic generation (SHG in 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole) DCNP molecule).[13] Furthermore, it was already proven that the size of nanocrystals can play a significant role on the excitation or emission efficiency of such organic systems.[14] Moreover such compounds can be also used for needs in ultrafast optics, i.e. as micro- or nanowaveguides in optical sensors[15].

Thus, motivated by the aforementioned properties of those materials, we performed a detailed investigation of a group of recently synthesized pyrazoline derivatives, which demonstrate an efficiently high nonlinear optical response. However, the main goal of this work is to highlight the capability of enhancing/modifying the optical nonlinearity by altering the molecular structure of these *push-pull* nanomaterials. In this respect, by keeping the electron donating part common and by changing the kind and position of the electron accepting part, we related the molecular structure with the nonlinearity, a property that can be of great importance in terms of their usability in photonic applications.

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Materials and methods

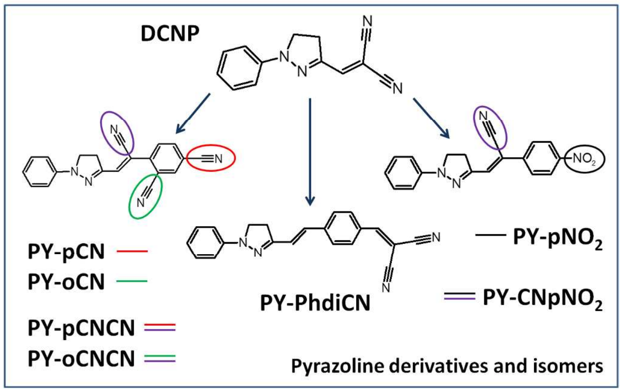

Figure 1. Chemical structures of all the investigated compounds. They are presented with the abbreviated names (full description in the text). During the NLO experiments we used thin PMMA films doped with one of the above dyes.

In this work the third order nonlinear optical response of eight compounds based on the pyrazole ring as a group of isomers and derivatives, which were synthesised by us according to the Knoevenagel and Fischer method[16,17] has been investigated (Fig. 1). After the synthesis all of the structures have been experimentally confirmed by H^1 NMR and IR spectroscopy, which was presented in the literature (cf ref. [17]). All of the molecules have the same electro donating (D) group (aromatic ring), but are differing in their electron acceptor part (A). As for example, in the first molecule of 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole molecule (abbreviated as DCNP), there are two nitrile groups positioned at the end of the structure. The two main parts (D - A) are connected with the pyrazole ring (electro donating region) by the ethenyl chain due to sustain the π–electron bridge between two opposite parts. The rest of the studied pyrazoline derivatives are also representatives of the *push-pull* type of molecular structures. The molecules can be separated in two different pairs of isomers, the (E)-2-(4-(1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)vinyl)benzonitrile (PY-pCN) and (E)-2-(2-(1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)vinyl)benzonitrile (PY-oCN) compounds, whose only difference is the location of a single electron acceptor substituent, which is a nitrile group, located at the end of the molecular structure in the *para* or *ortho* position, respectively. The second pair of isomers consists of the (Z)-2-(1-cyano-4-(1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)vinyl)benzonitrile (PY-pCNCN) and (Z)-2-(1-cyano-2-(1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)vinyl)benzonitrile (PY-oCNCN) compounds. They possess the same electron acceptor group positioned like in the two previous cases (*para* or *ortho* position), but this time the same nitrile group is located in the middle part of the compound. This fact causes different charge distribution along the structure. Moreover, in this work we present another two other compounds which are derivatives of the four previous ones. It is the (Z)-2-(4-nitrophenyl)-3-(1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)acrylonitrile - abbreviated as PY-CNpNO$_2$ and the (E)-3-(4-nitrostyryl)-1-phenyl-4,5-dihydro-1H-pyrazole compound (PY-pNO$_2$)). In this case a nitro group plays the role of the electron acceptor substituent instead of nitrile one. Additionally, at the former case first time in this case (the PY-CNpNO$_2$ compound) two different moieties are located in the same compound. Both last-mentioned molecules, are characterized by the presence of a nitro group, which is located in the *para* position at the end of the chemical structure. PY-CNpNO$_2$ possesses also a nitrile group positioned in the middle of structure, like the two previous ones (PY-oCNCN and PY-pCNCN). PY-pNO$_2$ molecule again possess only one electron acceptor group –NO$_2$, which is located at the end of structure in the *para* position. Finally, another molecule has been studied, the PY-PhdiCN one, which has a different structural form. It is similar rather to the DCNP, but it differs in terms of the additional aromatic ring and ethenyl chain. All the structural modifications arising from the molecular engineering imputation are expected to influence both the physicochemical parameters, like dipole moments, charge distributions, but also the nonlinear optical effects, like the third harmonic generation, and/or others studied in this work.

Experimental

The third order optical nonlinearities have been investigated by the Maker fringes set-up employing the fundamental exit (1064 nm) of a 30 ps Nd:YVO$_4$ laser with a repetition rate of 10 Hz at 532 nm. By means of a polarizer and a λ/2 wave-plate the polarization of the incident laser beam has been adjusted. The laser beam has been focused by a 250 mm lens on the sample which has been positioned near the focal plane, on a rotational stage. The latter allowed the variation of the angle of incidence with a step of 0.5 degrees. The beam size on the sample has been measured to be 300 µm and the energy per pulse was 40 µJ. By means of a KG3 filter the 1064 nm laser beam has been cut out, while with an additional interference filter at 355 nm, the third harmonic generated (THG) signal has been preserved and detected by a photomultiplier. The detected signal has been adjusted by appropriate neutral density filters, which have been positioned before the photomultiplier. The reference material during our measurements has been a fused silica slab with known nonlinear optical response $\chi_s^{(3)} = 2.0 \times 10^{-22} m^2 V^{-2}$.[18]

Due to the high linear absorption of the samples at the third harmonic generated wavelength (355 nm) we have used the following equation to analyse the experimental data:[1,19,20]

$$\chi^{(3)} = \frac{2}{\pi}\chi_s^{(3)} l_c^s \frac{\alpha/2}{1-exp(-\alpha l/2)}\sqrt{\frac{I_{3\omega}}{I_{3\omega}^s}} \quad (1)$$

where $\chi^{(3)}$, $\chi_s^{(3)}$ are the third order nonlinear susceptibilities of the sample and the reference material (silica in this case) respectively, l_c^s the coherence length of fused silica, l the film thickness, α the linear absorption coefficient, and $I_{3\omega}$ and $I_{3\omega}^s$ the peak intensities of the Maker fringes pattern of the film and the fused silica slab, respectively.

Results and discussion

For the needs of the NLO measurements thin polymeric films for each one of the investigated compounds have been prepared as follows. We used commercially available poly(methyl methacrylate) (M_w = 966 000 Da, Sigma Aldrich ®) in powder form and a series of pyrazoline derivatives which were described before. First of all proper solutions of PMMA/THF and PRD/THF were prepared. After mixing and heating for a few days when the polymer was completely dissolved, we mixed the mentioned solutions to make a final mixture (2 % dry weight proportion between pyrazoline derivative and polymer). In that way was easy to obtain a guest-host system, where the active material is stabilized by a fully transparent, well defined and long life polymer matrix. After mixing and heating the last-mentioned solution, the cleaned up silica glass plate was coated by a final mixture of PRD/PMMA/THF using the drop casting technique. The layers were drying during 3 days with solvent atmosphere until the evaporation process has finished. Then the thicknesses of the films have been measured by a profilometer (Tencor, ALFA-Step) and they are shown in Table 1.

The thickness has been found to be the same in several areas over the thin films verifying the high quality of the deposition. In Figures 2. and 3. representative UV-Vis-NIR absorption spectra of the samples are shown. As being evidenced in Fig. 2. the maximum value of the absorption of the three polymeric systems, which contain the DCNP, PY-PhdiCN and PY-pNO_2 molecules are very similar and located around 455 nm. Only one of them, the PY-CNpNO_2, characterizes maximum of the absorption band positioned a few nanometers to the longer wavelengths with comparison to the other ones. PY-PhdiCN which has the longest chemical structure and possesses the highest dipole moment value[16] exhibits an additional absorption band which is positioned close to the UV range. However, it is not observed at the figure because the curves were normalized to the maximum of the visible range and the UV spectral area has been cut.

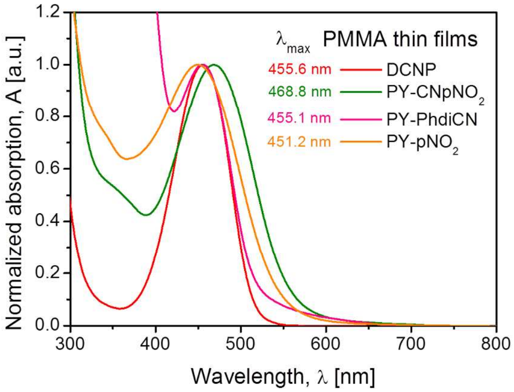

Figure 2. Normalized absorption spectra for the selected investigated polymeric systems (DCNP, PY-CNpNO_2, PY-PhdiCN, PY-pNO_2) obtained from the thin films.

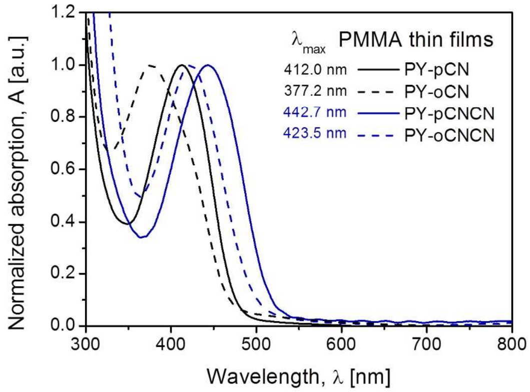

Figure 3. Normalized absorption spectra for the double pairs of isomers and derivatives of the investigated polymeric systems (PY-pCN, PY-oCN, PY-pCNCN, PY-oCNCN) in thin films.

In Fig. 3. the absorption spectra for the rest of the investigated systems, which are pairs of isomers and triples of derivatives, are presented. When comparing the PY-pCN and PY-oCN compounds, it is clearly visible that the position of the electro acceptor group has a great impact on the position of the spectral band. When the substituent is located at the end of the structure (*para* position) there is a red shift of about 34.8 nm. The same fact can be seen by comparing the PY-pCNCN and PY-oCNCN isomers, while in this case the spectral shift is equal to 19.2 nm. It should be also underlined that the application of a second electron acceptor group, in the middle part of the structure, also causes a red shift of the spectrum, respectively.

It is obvious that at 355 nm, where the third harmonic generation lies, there is significant linear absorption, which in any case has been taken into account during the analysis of the experimental data through the absorption factor of equation (1).

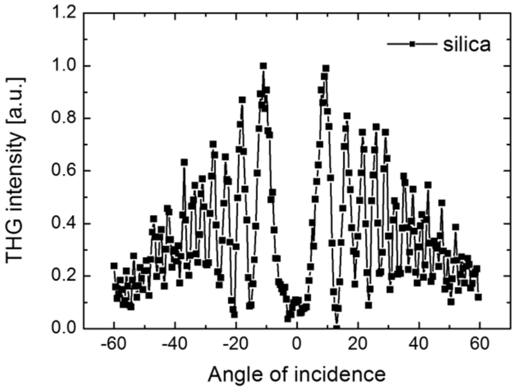

Figure 4. Characteristic third-harmonic generation Maker fringes of the reference sample (silica) obtained under 30 ps, 1064 nm laser excitation.

Table 1. Third order nonlinear optical parameters and thickness of the all of investigated thin polymeric systems (PRD/PMMA).

Sample	$\chi^{(3)}$ $(10^{-21}\ m^2/V^2)$	$\chi^{(3)}$ $(10^{-13}$ esu)	Thickness [μm]	α_0 $(10^3\ cm^{-1})$	$\chi^{(3)}/\alpha_0$ $(10^{-16}$ esu/cm$^{(-1)})$
DCNP	1.10	0.79	4.0	0.98	0.81
PY-PhdiCN	7.18	5.14	7.0	3.22	1.60
PY-pNO$_2$	8.14	5.83	4.5	5.12	1.14
PY-pCN	1.15	0.82	4.5	1.48	0.56
PY-oCN	1.04	0.74	4.2	3.67	0.20
PY-pCNCN	0.80	0.57	4.8	1.07	0.54
PY-oCNCN	0.81	0.58	4.5	0.82	0.71
PY-CNpNO$_2$	2.50	1.80	10.5	1.77	1.01

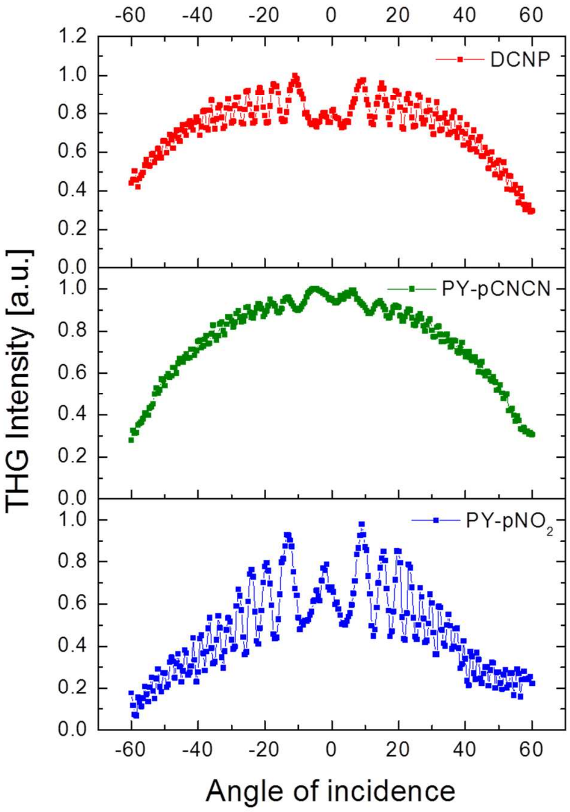

Figure 5. Characteristic third-harmonic generation signals of some of the examined *push-pull* compounds, obtained under 30 ps, 1064 nm laser excitation.

Concerning the nonlinear optical measurements, several Maker Fringes curves have been acquired in several zones over the samples. We have found that the obtained curves were similar all over the surfaces of the films verifying the homogeneity of the nonlinear optical response. Additionally the Maker fringes curve of the reference material have been acquired and are shown in Figure 4. In Figure 5. representative acquisitions can be seen for the molecules DCNP, PY-pCNCN and PY-pNO$_2$. By analysing the experimental data according to the equation (1) the third order nonlinear susceptibilities have been determined and shown in Table 1.

Due to the high linear absorption at the laser excitation wavelength the figure of merits ($\chi^{(3)}/\alpha_0$) are given for each film in the same table, in order to facilitate the direct comparison between the various compounds.

Several important conclusions can be drawn by comparing the third order susceptibilities and/or the figures of merits of the different molecular systems. Firstly, it can be seen that the highest values for both the $\chi^{(3)}$ and the $\chi^{(3)}/\alpha_0$ correspond to the PY-PhdiCN and PY-pNO$_2$ molecular systems. More specifically a comparison between the DCNP and the PY-PhdiCN shows that in the latter the $\chi^{(3)}$ and $\chi^{(3)}/\alpha_0$ values increase by a factor of 6.5 and 2, respectively. This clearly indicates that the longest conjugation length of the PY-PhdiCN system results in a higher delocalized electron cloud, which consequently enhances the third order NLO response. Another very interesting result arises by comparing two pairs of molecules - derivatives which different moieties (i.e. the (PY-pCN, PY-pNO$_2$) and the (PY-pCNCN, PY-CNpNO$_2$)). The molecules within each pair exhibit the same molecular structure except from the electron accepting moiety, which is either the nitrile unit or the nitro group respectively. It is clear that changing the acceptor part to -NO$_2$, results in both cases in a dramatic enhancement of the nonlinearity. On the contrary it seems that there is no clear relation between the location of the nitrile group (*ortho* or *para*) and the nonlinearity. By comparing the figure of merits it can be response compared with that of PY-pCNCN (despite of the lower value of α_0 of about 20 %). In both cases there is a slight modification of the $\chi^{(3)}/\alpha_0$ values between the *ortho* and *para* seen that the PY-oCN has a decreased nonlinearity compared with that of PY-pCN, while the PY-oCNCN has a little higher position, however we can conclude that this position change in low molecular mass systems does not induce a spectacular improvement on the nonlinearity.

Conclusions

In conclusion, in this work we report on 4-10 μm PMMA thin films, doped with a set of derivatives of pyrazole ring, which have been prepared by following the Knoevenagel and Fischer method, in order to be examined towards their third-order nonlinear optical response. For this, the third harmonic generation Maker fringes technique has been employed. The samples were excited with 1064 nm laser pulses, delivered by a 30 ps Nd:YVO_4 laser system. The *push-pull* molecular systems were consisting of an aromatic and pyrazole ring (electro donating part) and nitrile group(s) (electron acceptor part), resulting in different charge distribution of each molecular compound. In this respect, the nonlinear optical response of these molecules has been determined in two positions of the electron donating group (i.e., *para* and *ortho*). In addition, two derivatives of these molecules have been also examined, having a nitro group in *para* position connected to the aromatic ring in the acceptor region.

Presented studies clearly indicate that the longest conjugation length of the pyrazoline system enhances the third order NLO response. Additionally, it is clear that changing the acceptor part from –CN to –NO_2 results in a dramatic enhancement of the nonlinearity. Finally, it seems that there is no clear relation between the location of the nitrile group and the nonlinearity.

According to the experimental results, we can see that molecular engineering is an efficient way to manipulate the optical nonlinearities of such *push-pull* molecular systems.

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