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The third-order NLO properties of D- π -A molecules with changing a primary amino group into pyrrole

P. Audebert^{a,*}, K. Kamada^{b,1}, K. Matsunaga^b, K. Ohta^b

^a Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires, Ecole Normale Superieure de Cachan, 61 Avenue du President Wilson, 94235 Cachan Cedex, France

^b Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), AIST Kansai Center, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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Abstract

The nonlinear refractive index, as well as the two-photon absorption (TPA), has been investigated by the femtosecond Z-scan method for push-pull molecules, in which a primary donor group is weakened by conversion into a pyrrole or related heterocycle. The results at the fast response time show that, contrary to what had been expected from a previous work, there is a little decrease in the nonlinear refractive index change by introduction of the weaker donor groups. Although the measured TPA spectra showed that the observed nonlinear refractive index change was regarded to be off-resonant; difference in the frequency dispersion among the molecules considerably contributes to the decrease, in addition to difference in the intrinsic static nonlinearity. This shows that there is some future in the development of these non-resonant materials.

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1. Introduction

There has been an increasing amount of work on nonlinear optical (NLO) materials [1–5]. While the engineering for enhancing second-order NLO efficiency is relatively well understood and achieved, the need for efficient third-order molecules and materials still exists, especially for what

* Corresponding author. Fax: +33-1-4740-2454.

concerns materials exhibiting nonlinear refractive index change [6–11]. For such nonlinear optical molecules and materials, it is desirable to optimize the γ values, while keeping off-resonance for both one-photon and two-photon absorptions (TPA).

One of us (PA) published some time ago that it could be possible to increase the γ values while escaping resonance, simply by decreasing the strength of the donor group, in classical push-pull chromophores consisting of π -transmitter with electron withdrawing and donating groups at both ends [12]. Among such chromophores, two families of molecules had been investigated, where a primary amino group of the molecules in the first

E-mail addresses: pierre.audebert@ppsm.ens-cachan.fr (P. Audebert), k.kamada@aist.go.jp (K. Kamada).

¹ Also Corresponding author. Fax: +81-727-51-9637.

family {p-nitroaniline (PNA), p-cyanoaniline (PCA) and disperse orange 3 (DO3)} had been changed into an imide in the second one, while keeping the rest of the molecule (transmitter and electron withdrawing group) unchanged. The explanation proposed for the increase in γ of the molecules in the second family as the dipole moment of the molecule in the ground state was decreased, while the dipole moment in the excited state kept more or less the same value, which would lead to a neat increase of the γ value on the basis of a simple two-level model [13]. At that time, the measurements were performed by Z-scan technique with a 50-ps pulsed laser beam. With such a duration pulse, however, effects of nuclear motions including the orientational effect on the resultant γ value could not be completely excluded. In addition, the measurements had been made at the sole frequency of 1060 nm, which was of course off resonance for the molecules concerned, but the frequency dependence was not investigated.

It was therefore, worthwhile to extend this study, in order both to find the limits and possibly ameliorate our former interpretations, as well also to extend our investigations to new families of molecules. In our former study we measured and analyzed PNA, PCA, DO3 and their corresponding imides (designated as IPNA, IPCA and IDO3). In the present study, we describe new results on one of the former molecule PNA and its imide counterpart IPNA, as well as new molecules derived from PNA and DO3 by the conversion of the amino group into a pyrrole ring in the case of PNA and DO3 and a (1,5-bisthienyl)-pyrrole ring in the case of PNA (Scheme 1). As a matter of fact, conversion of the primary amino group into a pyrrole ring is another interesting way to diminish the donor strength since the nitrogen doublet becomes a part of the aromatic electrons of the pyrrole ring.

In this study, we have also investigated the TPA spectra, as well as the off-resonant nonlinear



Scheme 1. Molecular structures of the molecules studied.

refractive index, by the femtosecond Z-scan method for the molecules above. The reason of this is that it is essential to know the TPA spectra for evaluating the resonance enhancement of the real part of the γ value. Additionally the TPA property of the organic compounds is one of the current topics, and the present results could make some contribution to establishing the structure–property relation for such π -conjugated systems.

Furthermore, it should be remarked that not only the pyrrole (or oligopyrrole) rings act as electron withdrawing structures, but they can also serve as polymerizable groups, due to the wellknown electropolymerization of the pyrrole derivatives [14]. Therefore the intrinsic potential of such molecules is clearly beyond the initial goal, and they could well be the basis of new performing NLO polymers.

2. Experimental part

2.1. Synthesis of the molecules

PNA and DO3 are commercial compounds and were purchased (Aldrich Chemicals) and used without further purification. The synthesis of and IPNA was described before [12] and was performed according to the method of Toru and coworkers [15].

PYPNA (a previously known compound [16,17]) and PYDO3 were performed by the classical Paal–Knorr reaction, while TERPNA was prepared by extending a previously published procedure [18,19]. Typically, for the Paal–Knorr reaction the conditions were the following:

In a round-bottomed flask were introduced 4 mmol of the amino dye and 5 mmol of dimethoxytetrahydrofuran, with 20 ml of glacial acetic acid. The mixture is heated on an oil bath until it refluxes, after which the heating is immediately removed, and the content of the flask is poured on a mixture of sodium hydroxide and ice. After classical work-up with dichloromethane and chromatography (petroleum ether 1/dichloromethane 1), the desired compound is obtained (Rf = 0.7) with 60–70% yield. For TERPNA synthesis, the 1,4-dithienyl γ butyrodicetone [18,19] (1 g, 4 mmoles) and PNA (550 mg, 4 mmoles) were mixed in a round bottomed flask with *p*-toluenesulphonic acid (70 mg, 0.4 mmole), and refluxed for 14 h. Upon cooling, a solid was separated, which is usually pure TER-PNA. In order to obtain high purity compound, a purification chromatography is performed in dichloromethane/petroleum ether 1/1 mixture.

¹H NMR (350 MHz):

For PYPNA: 8.32 (dd, 2H, phenyl-NO₂); 7.52 (dd, 2H, phenyl-NO₂); 7.20 (t, 2H, α -pyrrole); 6.43 (t, 2H, β -pyrrole).

For PYDO3: 8.40 (m, 2H, phenyl-NO₂); 8.05 (t, 4H, phenyl-azo); 7.56 (d, 2H, phenylpyrrole); 7.20 (t, 2H, α-pyrrole); 6.40 (t, 2H, β -pyrrole).

For TERPNA: 8.23 (dd, 2H, phenyl-NO₂); 7.41 (dd, 2H, phenyl-NO₂); 7.15 (dd, 2H, α -thiophene); 6.87 (dd, 2H, β -thiophene); 6.56 (s, 2H, β -pyrrole); 6.55 (dd, 2H, β -thiophene). M⁺ = 352 (ionization).

2.2. Optical measurements

The sample solutions were prepared by dissolving the molecules in spectroscopic-grade dimethylsulfoxide (DMSO). The concentrations of the sample solution were adjusted so that the open aperture Z-scan signals could be detected (0.50 M for PNA and IPNA, 0.20 M for PYPNA, 0.32 M for TERPNA and 0.012 M for DO3 and PYDO3). The UV-Vis (one-photon) absorption spectra of the sample solution were recorded by a Shimadzu UV-3150 spectrometer. The sample solutions in high concentration were sandwiched between fused quartz plates and were used for the UV-Vis measurements. The optical path length of the solution film was adjusted in order to yield absorbance below 2. The recorded one-photon absorption spectrum of the solution film was little different from those of the diluted solution measured with a 1-cm quartz cuvette.

Third-order nonlinear optical properties of the sample solutions were measured by the Z-scan technique [20]. The optical setup is illustrated in Fig. 1. An optical parametric amplifier (*Spectra-Physics OPA-800*) pumped by Ti:sapphire regenerative amplifier system (*Spectra-Physics Spitfire*,



Fig. 1. Schematic outline of the femtosecond Z-scan setup. BS, beam sampler; QDP, quad-photodiode; CP, mechanical chopper; BPC, Berek polarization compensator; GTP, Glan-Laser prism; ND, neutral density filter; L, lens; S, sample; AP, iris aperture; PD, photodiode.

Merlin, Tsunami and Millennia) operating at the repetition rate of 1 kHz was used as light source. The output pulse width was 105-130 fs. The repetition rate used for measurement can be reduced without changing the beam property by mechanical choppers placed between the optical parametric amplifier and the measurement optics. A couple of quad-photodiodes were served to monitor the stability of beam position during the measurements. The sample solution in a 1-mm quartz cuvette was put on a power stage and was scanned along the optical axis. Three photodiodes connected to box-car averagers were used for signal detection. The closed and open aperture signals were corrected for nonlinear absorption and incident intensity as illustrated in Fig. 1. The closed aperture measurements were performed at the repletion rate of 10 Hz to suppress the accumulated thermal effect and the open aperture measurements were performed at 1 kHz. No spectral change of UV-Vis absorption was confirmed before and after the measurements of each sample.

2.3. Analysis of the Z-scan data

Both the open and closed aperture data were recorded in normalized transmittance as a function of sample position (z). The open aperture data was analyzed with TPA parameter q_0 defined as [21]

$$q_0 = \alpha^{(2)} (1 - R) I_0 L, \tag{1}$$

where $\alpha^{(2)}$ is the TPA coefficient, *R* is the Fresnel reflectance at the sample cell wall, I_0 is the on-axis peak intensity, and *L* is the optical path length of the sample cell. Eq. (1) holds for the measurements when the one-photon absorption is absent as in the present case. The parameter q_0 was obtained by curve fit using the relation [21]

$$T(\zeta) = \frac{(1-R)}{\sqrt{\pi}q(\zeta)^2} \int_{-\infty}^{+\infty} \ln[1+q(\zeta)\exp(-x^2)] \,\mathrm{d}x,$$
(2)

for the spatially and temporally Gaussian pulse along with $q(\zeta) = q_0/(1+\zeta^2)$. Here T is the normalized transmittance, $\zeta = z/z_R$ is the normalized z position, where z_R is the Rayleigh range. The z_R values were 3.5-6 mm for the measurements. We measured at least 4 different incident powers and confirmed that TPA is the dominant process for the observed nonlinear absorption by the linear relation between the obtained q_0 and I_0 shown as in Eq. (1). The TPA cross-section $\sigma^{(2)}$ is calculated from $\alpha^{(2)}$ with the relation $\sigma^{(2)} = h\omega\alpha^{(2)}/2\pi N$, where $h\omega/2\pi$ is the photon energy of the incident pulse and N is the number density of the solute molecule. I_0 was calculated from the incident pulse energy, the pulse width, and the beam waist radius calculated from $z_{\rm R}$.

The closed aperture data were analyzed with the difference between normalized transmittance at the peak and that at the valley, so-called ΔT_{pv} , which is proportional to the nonlinear index of refraction n_2 and the real part of the nonlinear susceptibility $\text{Re}[\chi^{\text{exx}}_{xxx}]$ as

$$\Delta T_{\rm pv} \propto n_2 I_0 L \propto \frac{I_0 L}{n_0^2} Re[\chi_{xxxx}^{(3)}],\tag{3}$$

where n_0 is the linear refractive index. We determined the $\operatorname{Re}[\chi_{xxxx}^{(3)}]$ of the sample solution with the $\operatorname{Re}[\chi_{xxxx}^{(3)}]$ of a high refractive-index glass (FD2) as reference material measured at the same experimental condition. The value of FD2 was determined based on that of fused silica [22]. We also measured a blank solution in the cell under the identical condition for each measurement and the contribution from the solvent and the cell walls were subtracted before calculating $\operatorname{Re}[\chi_{xxxx}^{(3)}]$. The real part of the second hyperpolarizability was calculated based on the relation

$$\operatorname{Re}[\gamma_{xxxx}^{(3)}] = \frac{\operatorname{Re}[\chi_{xxxx}^{(3)}]}{f^4 N},$$
(4)



Fig. 2. One-photon absorption (A) and TPA (B) spectra of PNA and IPNA. The curves in the panel B are just for eye guide.

where $f = (n_0^2 + 2)/3$ is the local field correction. In the following part, the symbols of Re[] and the suffix xxxx are omitted for simplification.

3. Results and discussion

3.1. Results on the nitrophenyl derivatives (PNA, IPNA, PYPNA and TERPNA)

First, the one- and two-photon absorption (TPA) spectra were measured because it was essential to know which wavelength region is nonresonant for further optical measurements. Figs. 2 and 3 display the results of TPA for both couples PNA/IPNA and PYPNA/TERPNA measured by the open aperture Z-scan method along with their one-photon absorption spectra. The TPA properties are also summarized in Table 1. Although the TPA peak of IPNA was not clear, the TPA bands for all the compounds except TERPNA are observed at approximately twice the wavelength of the lowest energy band of one-photon absorption,



Fig. 3. One-photon absorption (A) and TPA (B) spectra of PYPNA and TERPNA. The curves in the panel **B** are just for eye guide.

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Molecule	$\lambda_{\max, TPA}$ (nm)	$\sigma^{(2)a} \over (10^{-50} \ { m cm}^4 \ { m s})$	Im $[\gamma]^{b}$ (10 ⁻³⁶ esu)				
PNA IPNA PYPNA TERPNA DO3	~714 (<590) ~700 (<570) 932	$\begin{array}{c} 8.5 \pm 1.7 \\ (> 4.8 \pm 1.7) \\ 14.1 \pm 2.4 \\ (> 21.1 \pm 3.3) \\ 159.3 \pm 25.9 \end{array}$	$25 \pm 6.0 (>9.8 \pm 3.9) 40.6 \pm 8.3 (>40.2 \pm 7.8) 810 \pm 160$				
PYDO3	865	84.3 ± 11.4	370 ± 63				

Table 1 TPA properties of the molecules

^a TPA cross-section measured at 715, 595, 701, and 572 nm for PNA, IPNA, PYPNA and TERPNA, respectively. ^b Converted from the $\sigma^{(2)}$ values.

exhibiting that TPA transition shares the same excited state with one-photon absorption and no hidden TPA state exists below the excited state. Sharing the excited state with one- and two-photon transitions is reasonably explained in terms of molecular symmetry because the parity selection rule of one- and two-photon transitions breaks for asymmetric; structures like these molecules.

For IPNA, the TPA peak cannot be clarified due to the wavelength limitation of our experimental setup; however, the peak is estimated shorter than 600 nm, which is close to twice the one-photon absorption maximum (280 nm). The one-photon absorption and TPA peaks of IPNA are blue-shifted comparing to PNA and PYPNA. The blue shift of IPNA arises from rather weak electron donating ability of imide group than those of pyrrolyl and amino groups.

On the other hand, the TPA peak of TERPNA should be located at shorter than 570 nm and is not observed at twice the wavelength of the onephoton peak $(323 \times 2 = 646 \text{ nm})$. This suggests that the lowest TPA excited state of TERPNA must be different from the lowest one-photon excited state. For other three compounds, the directions of the transition moments of both oneand two-photon excited states are expected to be parallel to the phenylene-NO₂ axis. On the other hand, the TPA transition moment for TERPNA is not parallel to the phenylene-NO₂ axis, but parallel to the thienyl-pyrrolyl-thienyl axis. The corresponding one-photon excitation may be forbidden due to the symmetry property for the direction. The $\sigma^{(2)}$ maximum increased from PNA. to PYPNA and to TERPNA, which may correlate

to the molecular size and the charge transfer nature of the excitation concerned.

Second, the nonlinear refractivity of the compounds was measured by the closed aperture Zscan method. The second hyperpolarizability dominating the nonlinear refractive process $\gamma(-\omega)$; $\omega, \omega, -\omega$) is resonantly enhanced by only onephoton and two-photon absorptions [13]. The results of the above linear and nonlinear absorption measurements shows that there is no one- and twophoton absorptions at the wavelength longer than 900 nm for all the compounds. It is also needed to pay attention in near IR region for the overtone of IR absorption of the sample solution. In the case of DMSO, the overtones are observed at 1100-1200 nm and 1350-1500 nm. Therefore, the closed aperture Z-scan measurements at 1007 or 1016 nm can be regarded as off-resonant condition for the solvent as well as for all compounds. The obtained γ values are given in the Table 2. We can observe that weakening the donor group from amino (PNA) to pyrrolyl (PYPNA), to 2,5-dithienylpyrrolyl (TERPNA) and to maleimide (IPNA) results into a decrease in γ , contrary to what had been reported previously [12].

The second hyperpolarizability is often expressed by the following three-level model as

$$\gamma(0;0,0,0) \propto \frac{\mu_{01}^2 (\mu_0 - \mu_1)^2}{\omega_1^3} - \frac{\mu_{01}^4}{\omega_1^3} + \sum_n \frac{\mu_{01}^2 \mu_{1n}^2}{\omega_1^2 \omega_n}$$
(5)

Here ω_n is the transition energy between the ground and *n*th excited states, μ_{01} and μ_{1n} are transition moments between the ground and lowest excited states and between the lowest and *n*th excited states, respectively, and $\mu_0 - \mu_1$ denotes the

Molecule	Concentration (M)	$\lambda_{\max, OPA}{}^{a}$ (nm)	γ^{b} (10 ⁻³⁶ esu)
PNA	0.496	388	$+20.0\pm 6.01$
IPNA	0.499	288	$+3.79 \pm 2.13$
PYPNA	0.200	340	$+12.0 \pm 7.22$
TERPNA	0.0322	323	$+6.2 \pm 29.2^{\circ}$
DO3	0.0119	472	$+256\pm94^{\circ}$
PYDO3	0.0123	391	$+137\pm70^{\circ}$

Table 2Real part of off-resonant second hyperpolarizability

^a Wavelength of one-photon absorption maximum.

^b Here γ denotes the real part of the second hyperpolarizability, Re[γ]. Measured at 1007 nm for PNA and IPNA, at 1016 nm for PYPNA and TERPNA and at 1280 for DO3 and PYDO3. The signal from the solvent (DMSO) was subtracted. The convention used for γ is based on the power series as $\mu_{ind} = \alpha E + \beta EE + EEE$, where μ_{ind} is the induced dipole moment, α and β denote linear polarizability and first hyperpolarizability, respectively, *E* is microscopic electric field.

^c Large error due to low solubility.

difference in the dipole moments of the two states. This expression can be considered as the approximated formula of the following more complicated equation by ignoring the frequency factor ($\omega \rightarrow 0$).

$$\propto \frac{\mu_{01}^{2}(\mu_{0} - \mu_{1})^{2}\omega_{1}}{(\omega_{1}^{2} - \omega^{2})(\omega_{1}^{2} - 4\omega^{2})} - \frac{\mu_{01}^{4}\omega_{1}(\omega_{1}^{2} + \omega^{2}/3)}{(\omega_{1}^{2} - \omega^{2})^{3}} + \sum_{n} \frac{\mu_{01}^{2}\mu_{1n}^{2}\{\omega_{1}^{2}\omega_{n} + \omega^{2}(4\omega_{1} + \omega_{n})\}}{(\omega_{1}^{2} - \omega^{2})^{2}(\omega_{n}^{2} - 4\omega^{2})}.$$
(6)

However, for the present compounds like PNA, IPNA and PYPNA, where the TPA transition shares the same excited state with one-photon absorption and the molecule has a large dipole moment at the ground state, only the first term is expected to be dominant and can be employed for the analysis as in the previous paper ¹,

$$\gamma(-\omega;\omega,\omega,-\omega) \propto \frac{\mu_{01}^2(\mu_0-\mu_1)^2 \omega_1}{(\omega_1^2-\omega^2)(\omega_1^2-4\omega^2)}.$$
 (7)

Even if the γ values were measured at off-resonant conditions, we can expect enhancement in the γ values due to the frequency factor in the denominator of Eq. (7). Based on Eq. (7), we can estimate the enhancement factor compared to the static values at the limit of zero frequency using the following equation:

$$F = \frac{1}{\left[1 - (\omega/\omega_1)^2\right]\left[1 - (2\omega/\omega_1)^2\right]}.$$
(8)

The estimated frequency factors F for the present experimental optical frequency ($\omega \sim 9900 \text{ cm}^{-1}$) are 2.89, 1.62 and 2.04, for PNA, IPNA and PY-PNA, respectively, depending on the one-photon absorption peak positions (TERPNA is excluded because it does not seem to be suitable for this two-level analysis). By using the frequency factor, the static γ can be deduced as 6.9, 2.3 and 5.9 (in 10⁻³⁶ esu) for PNA, IPNA and PYPNA, respectively. Therefore, it is very probable that the decrease in the obtained y values from PNA to IPNA considerably arises from the frequency dispersion as well as the intrinsic static γ , originally from the blue shift of the one-photon absorption peak with weakened donor. Probably the previous two-level model may be too simplified to explain whole the observed results; nevertheless one can say that the transition moment factors in the numerator of Eq. (7) are estimated to be in the same order for all compounds.

This explanation can be supported by the recent ab initio molecular orbital calculation of the static γ value for PNA, IPNA and PYPNA [23]. The calculated results show that the static γ values for the three compounds are in the same order. Moreover the ab initio calculations reveal that both IPNA and PYPNA take the nonplanar structures by tilting the donating groups at the

¹ Eq. (7) is more rigorous equation than that in [12] as the term concerning the virtual transition path of 0-1-1-1-0.

optimized geometries. This should cause the partial disruption of the π -conjugated structures, which contributes to the blue shift of the absorption peak and also to decrease in the intrinsic static γ values despite the larger size of the molecules than PNA. Moreover, the calculation shows indications of possible contributions from the higher-excited states to the γ values for IPNA and PYPNA, which is not taken into account by the simple two-level model.

The previous interpretation that γ value increases with the weak donor group was a little optimistic. The previously observed increase in the γ value from PNA to IPNA [12] can be explained by taking the molecular orientational effect into account. The previous γ values were measured with 50-ps pulses, which is close to the rotational relaxation time of the molecule in solution. It is natural to expect that the rotational relaxation time of a strongly charge separated molecule like PNA becomes longer because of the interaction with the polar solvent molecules. If it is so, IPNA, which is a weaker charge-separated molecule, must have shorter rotational relaxation time than PNA and is guickly reoriented along the polarization direction of the incident pulse. Therefore, the anisotropic linear polarizability contributes to increase apparent γ value because usually the orientational contribution is much larger than the electronic contribution at room temperature. The previous γ values are probably the mixture of the orientational and electronic nonlinearities. This artifact can be neglected for the present measurements because the incident pulse width (\sim 110 fs) is two orders of magnitude or more shorter than the expected rotational relaxation times.

3.2. DO3 family compounds

Beyond DO3, only PYDO3 was accessible in this family, which is commercially available. Unfortunately TERDO3 (the analog of PYDO3 but with two thiophene rings substituted on the positions of the pyrrole ring like in TERPNA) was not accessible despite repeated attempts using various reaction conditions, the amino group of DO3 being definitely too weakly reactive. Fig. 4 represents both one-photon absorption and TPA spectra for both DO3 and PYDO3. Each maximum of TPA spectrum is located at almost twice the wavelength of the corresponding onephoton absorption maximum. The maxima of $\sigma^{(2)}$ values of DO3 and PYDO3 were larger than those of the nitrophenyl derivatives, exhibiting the effect of longer conjugation length in DO3 family. At the wavelength longer than 1200 nm, there is no TPA for both DO3 compounds and no overtones of IR absorption of the solvent, so the closed aperture Z-scan measurements were performed at 1280 nm.

The obtained γ values at the wavelength are $(+256 \pm 94) \times 10^{-36}$ esu for DO3 and $(+137 \pm 70) \times 10^{-36}$ esu for PYDO3 as also shown in Table 2. These γ values are much larger than those of the nitrophenyl derivatives, reflecting the larger molecular size and π -conjugation length. This result shows the trend similar to the previous results for the nitro series, again corresponding to the one-photon peak positions.



Fig. 4. One-photon absorption (A) and TPA (B) spectra of DO3 and PYDO3. The curves in the panel **B** are just for eye guide.

If we apply the similar discussion concerning frequency factors for DO3 and PYDO3 as done for the PNA series, the estimated frequency factors F (Eq. (8)) for the experimental optical frequency ($\omega \sim 7800 \text{ cm}^{-1}$ in this case) are 2.54 and 1.76 for DO3 and PYDO3, respectively. Then the static γ values are deduced as 101 and 78 (in 10^{-36} esu) for DO3 and PYDO3, respectively. Therefore, DO3 still seems to have a larger γ value than PYDO3 at the static limit, although the two values become close to each other. Again this is probably caused by the fact that PYDO3 contains a much weaker donor group (pyrrolyl) than DO3 does (amino), and the presence of the pyrrolyl group may disrupt the π -conjugation.

4. Conclusion

We have described the preparation and the third-order NLO properties in the femtosecond range of two families including new molecules possessing the same withdrawing group and π connecting system and donor groups with various strength. The results show that the γ (real part) measured at the off-resonant wavelength decreases as the decreasing strength of donor group in spite of the expectation from the previous results. The measurements of TPA and one-photon absorption spectra exhibited that both of the lowest energy TPA transition and the one-photon transition shared the same initial and final states, except for TERPNA. The analysis based on the simplified two-level model considering the ground and lowest excited states suggested that the variation of measured γ among the molecules is governed not only by the intrinsic static γ but also by the frequency dispersion. Thus, decreasing the donor strength increases the transition energy between the two states, and then decreases the frequency factor at the observation wavelength even if it is in the off-resonant region. The present results suggested that not only optimizing of the static γ but also tailoring the transition energy relating with the frequency factor at the wavelength in use is important for the future applications.

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