Chemical dynamics and reverse saturable absorption in di-furfuryl ether solutions

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Abstract

We report on the chemical dynamics and nonlinear optical absorption of di-furfuryl ether (DFE) solutions. DFE molecules were derivatized from the room temperature furfuryl alcohol self-reaction, whose reaction kinetics was investigated with the Z-scan technique and laser-induced fluorescence. These molecules are shown to exhibit a pronounced reverse saturable absorption process. The magnitude of the excited-state absorption cross-sections and the intersystem crossing lifetime have been evaluated with 8 ns pulses at 532 nm. © 2001 Published by Elsevier Science B.V.

1. Introduction

Organic materials have attracted considerable interest because their large nonlinear susceptibilities and fast response times are promising for use in optical signal processing devices [1–3], and also due to their potential application as passive optical limiters to protect sensors and eyes from intense light pulses [4]. Among organic materials, π-conjugated polymers such as poly(aniline), poly(thyophene) and poly(furylene vinylene) have been the subject of extensive theoretical and experimental investigation aiming at understanding and improving their design, synthesis and optical properties [5]. A class of π-conjugated systems containing furan rings in the backbone have also received considerable attention because they are employed to synthesize polymers and resins that can be used in coating processes [6,7]. This family

of compounds is based on the furfuryl alcohol (FA), a natural and renewable source of monomers that originates from the chemical transformation of polyoses present in corn-cobs, cotton, rice-husk and sugar-cane [8,9]. Although FA conjugated polymers constitute a new class of conductive materials with potential technological applications [10,11], their most interesting properties cannot be fully explored because the backbone usually presents ramifications that are deleterious to the linear conjugation [6,7]. Therefore, the understanding of the FA polymerization reaction, which is assisted by the condensation induced by an acid [12], is important to avoid the ramification mechanism, whose reduction could lead to the improvement of the polymer's conductive and mechanical properties. Moreover, the control of the oligomer's size [13], and consequently of the conjugation length, could allow the enhancement of the nonlinear optical response. In the course of investigations on the ramification mechanism, we verified the presence of molecules arising from a self-reaction process that could

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affect the polymerization evolution. Besides, we casually found that the self-reaction product presents a strong saturable absorption (RSA) mechanism. This observation motivated us to investigate in detail the formation of derivatized molecules arising as consequence of the FA self-reaction and their behavior as passive optical limiters. The use of several analytical techniques allowed us to identify the newly formed species as the di-furfuryl ether (DFE) and its function isomer, 5-furfuryl-furfuryl alcohol (5FFA). In order to gain further insight on the self-reaction process, we employed the Z-scan technique with Fourier analysis [14] and laser-induced fluorescence (LIF) to study its kinetics. To our knowledge, this is the first time that the sensitive nonlinear Z-scan technique was used to follow the time evolution of a chemical reaction. With the combination of these two techniques we can monitor the presence of different products during the FA self-reaction; while the Z-scan measurement detects all types of molecules that absorbs in the visible and give rise to thermal lensing, the LIF measurement is more selective because it detects just the DFE. We were also able to find that in a later stage, DFE molecules combine to form tetramers in such way that their concentration remains constant. Finally, we performed nonlinear absorption measurements to analyze the reverse saturable absorption process in DFE molecules, which is an important feature for the manufacture of optical limiting devices.

2. Experimental

The commercially available furfuryl alcohol (Sigma-Aldrich) was purified by low-pressure distillation, resulting in a colorless liquid that was subsequently dried in Na_2SO_4. Soon after, the infrared absorption and ^{13}C-NMR spectra were, respectively, measured with a Bomem-Mb102 and a Brucker UX-200 spectrometers. The results obtained were identical to those already reported in the literature [6,7], meaning that we are indeed working with the pure FA schematically shown in inset of Fig. 1. UV-Vis spectra were obtained with a Hitachi U2001 spectrometer, with the solution placed in a 2 mm quartz cell, while emission
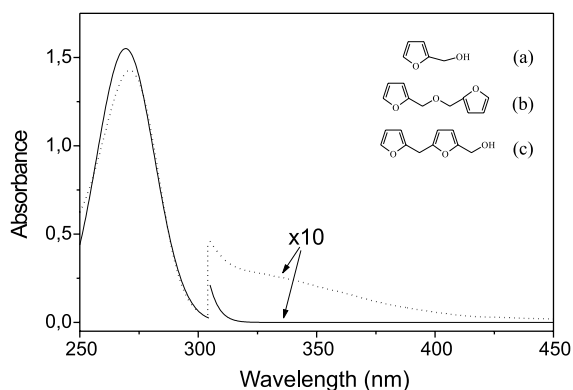

Fig. 1. Absorbance ($-\log_{10}(I/I_0)$) spectra of freshly distilled FA (solid line) and after aging for several days at room temperature (dashed line). The inset shows molecules of FA (a), DFE (b) and 5FFA (c).

spectra were measured with a Hitachi F-4500 fluorescence spectrometer, by pumping the sample with light at 500 nm. In order to identify the derivatized molecules arising at the earlier stage of the self-reaction process, we carried out chromatographic analyses with a Shimadzu GC-17A, using hydrogen as the mobile phase and thermal conductive detection (TCD) in column DB1, and mass spectrometry performed in a Shimadzu GC-MS QP5000.

The self-reaction kinetics was studied with both LIF and Z-scan techniques. The former uses an argon ion laser operating at 514.5 nm to excite the sample. The resulting fluorescence is collected by a 15 cm focal length lens and filtered by a high-pass filter placed in front of a photomultiplier tube to collect the wavelength-integrated signal. On the other hand, the Z-scan technique [15] was used as a probe for non-luminescent molecules. Basically, the method consists in translating the nonlinear sample through the focal plane of a tightly focused Gaussian beam and monitoring the changes in the far field intensity pattern. For a purely refractive nonlinearity, the light field induces an intensity dependent nonlinear phase and as consequence of the transverse Gaussian intensity profile, the sample presents a lens-like behavior. The induced self-phase modulation has the tendency of defocussing or recollimating the incident beam, depending on its z position with respect to the focal

plane. By monitoring the transmittance change through a small circular aperture placed at the far-field position, one is able to determine the nonlinear refractive index, n_2. Any nonlinear absorption present at the sample can be found in a measurement where the aperture is removed. However, our samples did not present any nonlinear absorption when exposed to a low power cw laser beam and we restricted our measurements to the nonlinear refractive index.

For the present measurements, we employed the Z-scan technique with Fourier analysis [14,16] to investigate the nonlinear refractive index of the FA solution. The experimental setup is fully described in [14] and only a few details are presented here. As light sources we have used an argon ion laser (488 and 514.5 nm) and a cw dye laser operating with rodhamine 590 (570–615 nm). The laser beam is modulated at a frequency f with a mechanical chopper and the transmission through the aperture located at the far field is monitored as a function of the sample z-position. The Fourier components at f and $2f$, measured with two independent lock-ins, are respectively, related to linear and nonlinear refraction, and their ratio, $R(z,f)$, allows to eliminate spurious linear effects. The dependence of R on f can be used to distinguish nonlinear processes with different relaxation times and allows the determination of the thermal diffusion coefficient in thermal processes.

Nonlinear absorption measurements were carried out with a Q-switched Nd:YAG laser producing 8-ns-duration (FWHM) pulses at 532 nm. The beam with a 3 mm diameter was transmitted through a 10 mm quartz cell containing a dilute solution of DFE (3×10^{-4} M) in dichloro-methane (DCM). The transmission was characterized as a function of the input laser fluence by rotating the first of two Glan laser-polarizers placed in front of the cell.

3. Results and discussion

3.1. Derivatized molecules characterization

The UV-Vis spectrum for freshly distilled FA is depicted in Fig. 1. It presents just a broad ab-

sorption band centered at 270 nm, which is known to be related to the furan ring π–π^* transition [12]. However, when the solution ages for several days at room temperature and illumination, it presents a bathochromic shift due to its self-reaction [6,9], as shown by the dashed line in Fig. 1. By means of chromatographic analyses carried out after 6 h of aging, we found 99.56 wt% of pure FA, but we also found 0.30 and 0.14 wt% of two other compounds. These unknown compounds were isolated and concentrated to have their masses determined. The resulting fragmentation spectra are similar to those reported in [17,18], and the structures observed were directly associated with the DFE and its function isomer, 5FFA, both shown in the inset of Fig. 1.

Each isolated compound was diluted in DCM to allow the transmission of light through the sample, which otherwise would be opaque at the UV region. The UV-Vis spectra of the isolated compounds show that only DFE molecules absorb appreciably in the visible, as depicted in the left-hand side of Fig. 2. This spectrum can be deconvoluted and results in three bands centered at 275, 340 and 400 nm, as shown by dashed lines in the figure. On the other hand, the 5FFA presents negligible absorption in the visible and the only important band observed was associated to the furan ring π–π^* transition lying at the ultraviolet. The light absorption by DFE molecules results in fluorescence emission, whose lineshape strongly
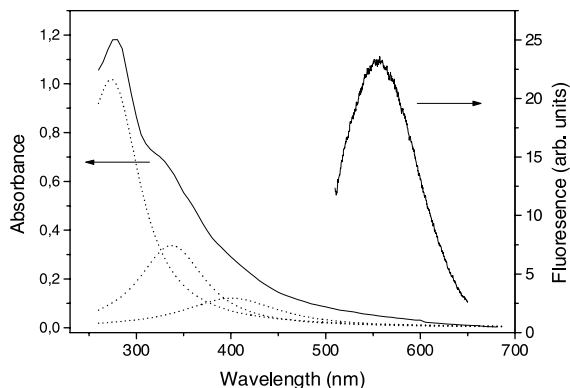

Fig. 2. Absorbance ($-\log_{10}(I/I_0)$) and fluorescence spectra of DFE in a DCM solution. This particular emission lineshape is obtained for excitation light at 500 nm.

depends on the excitation wavelength due to the existence of three absorption bands. As an example, the right-hand side of Fig. 2 shows the emission spectrum obtained when the sample is pumped by light at 500 nm, which excites just the tail of the longer wavelength absorption band. When the excitation is performed at 450 nm, two emission bands are observed. On the other hand, since the absorption of the 5FFA molecule is negligible at the visible, no fluorescence is observed. Accordingly, when the aging FA solution is exposed to light from an argon ion laser operating at 514.5 nm, the fluorescence intensity can be used to determine the number of DFE derivatized molecules. However, since the aging sample contains mostly FA, we have to make sure that the emission is not related to a direct π–π^* transition due to a possible two-photon absorption process occurring in these molecules. For this purpose, we measured the fluorescence intensity as a function of the argon laser power. The linear behavior observed indicates that no two-photon process is present and the fluorescence can be attributed to a small amount of DFE molecules absorbing and emitting in the visible region.

3.2. Z-Scan measurements

As we just mentioned, LIF can be used to monitor the number of DFE derivatized molecules because they have a sufficiently high fluorescence quantum yield. On the other hand, the Z-scan technique was chosen as a probe for non-luminescent molecules because of its high sensitivity to measure any light-induced refractive index change. To determine the origin of the nonlinear index, we performed a set of Z-scan measurements at 514.5 nm with different modulation frequencies. We used a FA sample that aged for 6 h after distillation, as in the chromatographic analysis. The observed nonlinearity is negative ($n_2 < 0$), which is typical for thermal nonlinearities in liquid samples. Fig. 3a shows the dependence of the peak and valley separation, ΔZ_{pv}, on the modulation frequency. The solid line represents a function $f^{-1} +$ constant, used to fit the data as in [16]. This dependence indicates that the nonlinear effect has indeed a thermal origin. For low modulation fre-
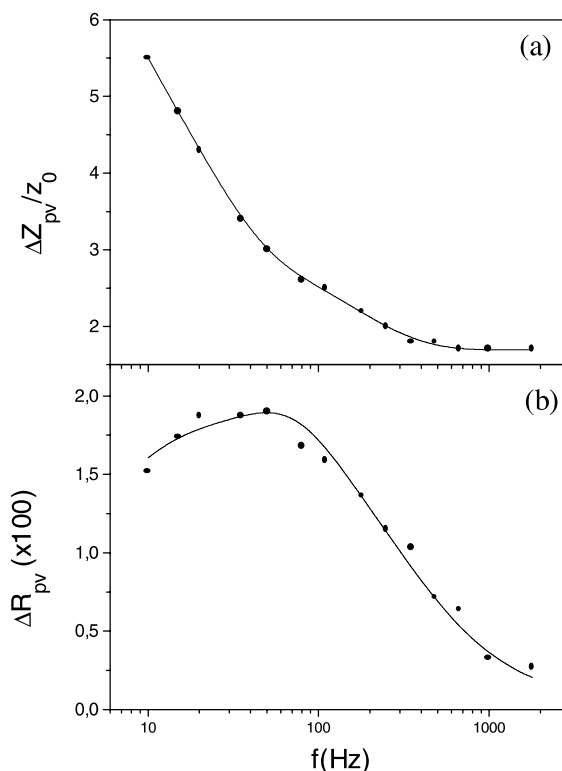

Fig. 3. (a) Dependence of ΔZ_{pv} on the chopper frequency and theoretical fit (solid line) with a function $50/f + 1.7$ and (b) ΔR_{pv} versus the modulation frequency and theoretical fit (solid line) provided by Eq. (4) of [14]. The excitation wavelength is 514.5 nm.

quencies, the heat diffusion is considerable and the thermally induced lens becomes broader than the Gaussian profile of the incident beam, resulting in a larger ΔZ_{pv}. However, at the high frequency regime there is not enough time for the heat diffusion to occur and the thermal lens follows the Gaussian profile of the beam. In this case, ΔZ_{pv} is narrower and tends to the value 1.7 z_0, predicted by Sheik-Bahae et al. [15] as the frequency becomes much larger than the inverse of the thermal relaxation time. Defining ΔR_{pv} as the difference of $R(z, f)$ between the peak and valley positions, we measured the dependence of ΔR_{pv} on f, as shown in Fig. 3b.

The thermal diffusion coefficient, $D = K_T/\rho C_p$ (K_T being the thermal conductivity, ρ the mass density and C_p the heat capacity) and the nonlinear refractive index, n_2th, can be obtained using Eq. (4)

of [14]. We found $D = 7.0 \times 10^{-4}$ cm^2/s, which is in good agreement with values presented in the literature for the pure furfuryl alcohol ($K_T = 4.28 \times 10^{-4}$ cal cm^{-1} s^{-1}, $\rho = 1.12$ g cm^{-3} and $C_p = 0.502$ cal g^{-1} °C^{-1}) [19], and the thermal nonlinear index as n_2th $= -6.9 \times 10^{-7}$ cm^2/J.

The thermal lensing monitored by the Z-scan technique can be attributed to species formed during the FA self-reaction, which are responsible for the absorption of light and subsequent heat generation. We have also carried out Z-scan measurements as a function of the wavelength to confirm the thermal origin of the observed effect. We observed that n_2 enhances in the blue region where the energy of the incident photon increases, as expected for a thermal nonlinearity arising from a radiative processes. As the light frequency increases, the quantum efficiency becomes smaller and the excess energy carried by the photon is converted into heat.

3.3. Self-reaction kinetics

The concentration and number of species depends on the FA aging stage. After several days or weeks, a large number of different species are produced and this makes the analysis quite complex. However, we are interested in the initial stage of degradation, where just the two compounds observed in gas chromatography are present and are responsible for the optical process observed. As the self-reaction evolves, the concentration of derivatized molecules increases in a way that we want to characterize. As discussed previously, the 5FFA is invisible to the optical probes employed because it neither absorb nor emit when pumped by 514.5 nm light. Therefore, both Z-scan and fluorescence signals are proportional just to the concentration of DFE. Fig. 4(a) shows that the fluorescence intensity increases linearly for the first 110 h of aging and after that it becomes constant. From the chromatographic analysis carried out after 6 h of aging we estimate that the fluorescence stabilizes at a DFE concentration corresponding to about 5 wt% of that of FA. Fig. 4b presents the time evolution of ΔR_{pv}, measured at $f = 50$ Hz. In this case, the signal always increases linearly in time, but two different growth rates can be clearly
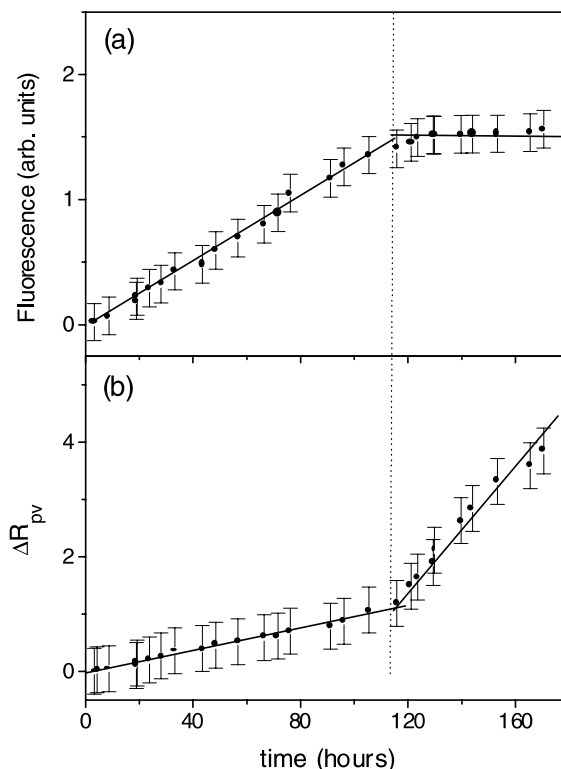

Fig. 4. (a) Fluorescence and (b) Z-scan signal in an FA sample aging at room temperature. The excitation wavelength is 514.5 nm.

observed. The time for which the Z-scan signal changes its growth rate corresponds to that where the fluorescence intensity becomes constant.

To explain this behavior, we propose a model where two molecules of FA initially combine to produce either one DFE or one 5FFA molecule. The linear increase in the DFE concentration observed in both probe signals is related to the fact that the concentration of FA is not depleted because the amount of derivatized molecules is small. The rate equation describing the time-evolution of the DFE concentration is given by:

$$\frac{d[N_{DFE}]}{dt} = k_1 [N_{FA}]^2, \tag{1}$$

where $[N_{DFE}]$ and $[N_{FA}]$ are, respectively, the DFE and FA concentrations, and k_1 is the rate constant for dimerization. Assuming that the N_{FA} concentration is constant, we obtain the linear time-

dependent behavior as $[N_{DFE}] = k_1[N_{FA}]^2 t$. Additional terms accounting for the reaction between DFE and FA, and between two DFE are not considered because they would produce a nonlinear time-dependence, which clearly does not reproduce our results. Since the DFE concentration clamps at about 5% after 110 h, we can estimate the value of k_1 as being 7×10^{-9} l mol^{-1} s^{-1}.

After a critical concentration of dimers is reached, new reactions will take place, but in this case, the newly formed DFE and 5FFA are reactants and not products as in the earlier case. In this second stage of the self-reaction, the new compounds originating from the dimers structures stabilize the DFE concentration, as seen in the fluorescence signal depicted in Fig. 4(a). The increase in the growth rate of the Z-scan signal may have two origins. First, the new derivatized molecules could have an absorption coefficient higher than DFE, but we do not have a way to confirm this because the absorbed light fraction is always very small and cannot be detected. Second, and probably more important, since the tetramers formed do not fluoresce, the heat emitted through radiationless transitions is much higher and the thermal lensing is more notable. The rate equation for the DFE concentration in this second stage is more complex because we have, in principle, to take into account the reaction between two DFE, and between one DFE and one 5FFA. Again, we do not consider the reaction between DFE and FA because it already did not exist in the first stage. Therefore the new rate equation is:

$$\frac{d[N_{DFE}]}{dt} = k_1[N_{FA}]^2 - k_2[N_{DFE}]^2 - k_2'[N_{DFE}][N_{5FFA}] = 0,$$

(2)

where k_2 and k_2' are rate constants for the DFE reaction, and just the stationary case was considered because the fluorescence intensity is constant. Eq. (2) cannot be directly solved because we do not know the time-evolution of $[N_{5FFA}]$ and neither if becomes constant after the first hundred hours. However, in order to make a rough estimate of k_2, we will neglect the last term in Eq. (2), which lead us to the ratio $k_2/k_1 = 900$. This means that the self-reaction of DFE is more effective than that of FA.

3.4. Reverse saturable absorption

The fluence-dependent transmission of the dilute DFE/DCM solution is represented by full circles in Fig. 5. This result can be explained by the five-level model depicted in the insert, where the relaxation from T_1 to S_0 is neglected because it is much longer than the 8 ns pulse duration. The upper excited singlet and triplet levels S_n and T_n are assumed to be too short-lived to present any population build up. The rate equations used to describe the population densities, n_i ($i = 0$, 1 and 3), at each level are:

$$\frac{dn_0}{dt} = -n_0 W_{01} + \frac{n_1}{T_{10}},$$

(3)

$$\frac{dn_1}{dt} = n_0 W_{01} - \frac{n_1}{T_{10}} - \frac{n_1}{T_{isc}},$$

(4)

$$\frac{dn_3}{dt} = \frac{n_1}{T_{isc}},$$

(5)

where $W_{01} = \sigma_{01} I / h\nu$ is the transition rate for $S_0 \rightarrow S_1$, with σ_{01} being the ground state cross-section and I the intensity. T_{10} is the lifetimes of level S_1 and T_{isc} is the intersystem crossing lifetime. This set of equations was numerically solved using a Gaussian temporal intensity profile for the Q-switched pulse used in our experiment, yielding the population dynamics, $n_i(t)$. The time evolution
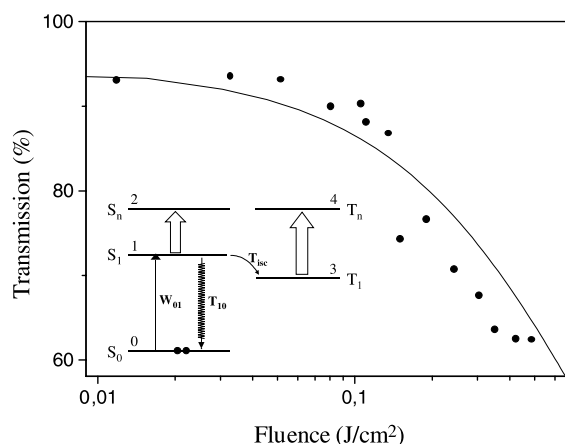

Fig. 5. Fluence-dependent transmission of the dilute DFE/DCM solution (full circles) and theoretical fitting with the parameters given in the text (solid line).

of the nonlinear absorption was calculated according to:

$$\alpha(t) = N\{n_0\sigma_{01} + n_1\sigma_{12} + n_3\sigma_{34}\}, \tag{6}$$

where N is the DFE concentration, and σ_{12} and σ_{34} are the excited state cross-sections. σ_{01} was determined by measuring the linear absorption at 532 nm ($\alpha_0 = N\sigma_{01}$, with $N = 2.5 \times 10^{17}$ cm^{-3}) resulting in $\sigma_{01} = 3.5 \times 10^{-19}$ cm^2. The numerical calculation was carried out with $T_{10} = 2.7$ ns, obtained through time-resolved fluorescence measurements. The solid line in Fig. 5 represents the theoretical fitting obtained with $\sigma_{12} = 7.5 \times 10^{-19}$ cm^2, $\sigma_{34} = 9 \times 10^{-17}$ cm^2 and $T_{\mathrm{isc}} = 150$ ns. The intersystem crossing lifetime is almost 10 times higher than those of other organic molecules traditionally investigated for optical limiting purposes [20,21]. However, this time could be lowered with the introduction of a metal atom to increase the spin-orbit interaction. On the other hand, the ratio between the excited and ground states cross-section is nearly 200, a factor of 10 higher than in metallophthalocyanines and tetrabenzophyrins, which is quite convenient for optical limiters. We are presently characterizing the dynamic optical nonlinearities in DFE solutions with the Z-scan technique with pulse trains [22].

4. Conclusions

We have employed gas chromatography and mass spectroscopy to determine the derivatized molecules arising at the earlier stage of the FA self-reaction. Then, we used two complementary optical probes to analyze the kinetics followed by the self-reaction. LIF measurement permitted a direct determination of the DFE concentration while the non-selective Z-scan technique monitored the thermal lensing arising as consequence of the absorption of any derivatized molecules in the wavelength used. It also provided information on the thermal properties of the FA. Although an equivalent method has already been used to sense the thermal lens in a chemical reaction [23], this is the first time that the Z-scan technique is employed for this purpose. The presence of DFE molecules and its high reaction rate may be deleterious to the polymerization process. However, owing to the low vapor pressure of ethers, DFE molecules can be removed if the polymerization is carried out in vacuum. We already tried this approach and obtained good results that will be published elsewhere.

Finally, the nonlinear optical absorption of a DFE/DCM solution was investigated with 8 ns pulses at 532 nm. The sample presented an RSA process and the magnitude of the excited-state absorption cross-sections as well as the intersystem crossing lifetime have been evaluated.

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