

# Push-pull chromophores aggregation in SiO<sub>2</sub> sol-gel films doped with silver nanoparticles

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Sol-gel films used for second-order non-linear optical applications often contain some organic molecules working as spacers between chromophores with large permanent dipolar moments. The spacers improve the optical quality of the films because they avoid the chromophores aggregation. We propose the use of silver nanoparticles as good spacers, instead of organic molecules. In this work the effect of silver nanoparticles on the arrangement of push-pull chromophores inside SiO<sub>2</sub> sol-gel films is investigated by UV-vis optical absorption spectroscopy. Key variables for a good performance of spacers are: their polarizability, their concentration with respect to the concentration of the chromophores, as well as the temperature of the system. Disperse Red 1 chromophores, well known push-pull chromophores, arrange themselves forming H-aggregates when they are inside films in high enough concentrations. Those aggregates are clearly detected by UV-vis optical absorption spectroscopy, where they show an absorbance peak close to 404 nm. That peak disappears as the temperature of the films and/or the concentration of the spacers and/or the polarizability of the spacers increase. A possible electrostatic shielding between the chromophores, created by the spacers, makes us to think about the possibility to use metallic nanoparticles as a new kind of molecular spacer.

**Keywords:** Sol-gel films; metallic nanoparticles; molecular aggregation; UV-vis spectroscopy; push-pull chromophores.

Las películas sol-gel empleadas para aplicaciones en óptica no lineal de segundo orden frecuentemente contienen moléculas orgánicas que funcionan como espaciadores entre cromóforos que tienen momentos dipolares permanentes grandes. Los espaciadores mejoran la calidad óptica de las películas porque evitan la agregación de cromóforos. Nosotros proponemos el uso de nanopartículas de plata como buenos espaciadores, en vez del uso de moléculas orgánicas. En este trabajo se investiga el efecto de las nanopartículas de plata sobre el arreglo de cromóforos push-pull dentro de películas sol-gel de SiO<sub>2</sub> por medio de espectroscopia de absorción óptica UV-vis. Las variables clave para un buen desempeño de los espaciadores son: su polarizabilidad, su concentración en relación a la concentración de cromóforos, así como la temperatura del sistema. Los cromóforos Disperse Red 1, cromóforos push-pull bien conocidos, se acomodan por sí mismos formando agregados H, cuando se encuentran dentro de películas en concentraciones suficientemente grandes. Tales agregados son detectados claramente mediante espectroscopia de absorción óptica UV-vis, en donde exhiben un pico de absorción cercano a los 404 nm. Dicho pico desaparece conforme la temperatura de las películas y/o la concentración de los espaciadores y/o la polarizabilidad de los espaciadores aumentan. Un posible apantallamiento electrostático entre los cromóforos, creado por los espaciadores, nos hace pensar en la posibilidad de usar nanopartículas metálicas como un nuevo tipo de espaciador molecular.

**Descriptores:** Películas sol-gel; nanopartículas metálicas; agregación molecular; espectroscopia UV-vis; cromóforos push-pull.

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## 1. Introduction

Sol-gel films doped with organic push-pull chromophores are potential candidates for photonics applications due to the ease of their fabrication and their good optical performances [1,2]. However, they have some features to overcome: the small amount of chromophores that sol-gel films can host and their stability. In particular, for second-order non-linear optical applications the stability means to maintain the chromophores oriented non-centrosymmetrically inside the material. Due to the fact that push-pull chromophores usually have large permanent dipolar moments, they tend to form aggregates, in consequence they do not distribute homogeneously in the materials when their concentration is high. Also, if the chro-

mophores are oriented in a particular way inside a matrix, they tend to loose their orientation because of dipole-dipole interactions [3]. For blocking the strong dipole-dipole interactions between chromophores it is common to incorporate other kind of organic molecules in the materials, as the carbazole moieties, in order to increase the quantity and stability of the push-pull chromophores inside the materials [4]. We use silver nanoparticles as a novel kind of inorganic spacers between chromophores.

The existence of surface plasmons in metallic nanoparticles indicates that they are highly polarizable moieties, thus they should be able to block efficiently the interactions between chromophores. It means that metallic nanoparticles should be able to avoid the formation of push-pull chro-

mophores aggregates and to increase the stability of the chromophores orientation.

In this work we present the physical mechanism behind the molecular spacers, the synthesis of sol-gel films doped with push-pull chromophores and metallic nanoparticles, the detection of surface plasmons and molecular aggregated states in the films by means of UV-vis optical absorption spectroscopy, and finally we analyze and discuss the results.

## 2. Physical model

When a material has a very low chromophores concentration, the chromophores are homogeneously distributed inside the material, the distance between them is very large and the dipole-dipole interactions are negligible. Therefore, at low chromophores concentrations it is not necessary to use spacers in order to avoid aggregation. But as the chromophores concentration increases in a system, the distance between chromophores decreases, the dipole-dipole interactions become larger and different kinds of aggregation structures take place. Then the use of spacers becomes necessary in order to avoid the aggregation of the chromophores.

Some molecular spacers decrease the dipole-dipole electrostatic interactions existing between push-pull chromophores by the means of the induction of an electrostatic shielding between neighbor chromophores. It means that the large permanent dipole of the push-pull chromophores induce dipoles in the spacers, which screen the interaction between the permanent dipoles of neighbor chromophores.

An induced dipole  $p$  in a spacer is directly related to the polarizability of the spacer  $\vec{\alpha}$  and to the external electrostatic field  $E$  in which the spacer is immersed by means of the equation:

$$p = \vec{\alpha} E \quad (1)$$

Thus, as the components of the polarizability are larger, the induced dipoles in the spacers should shield better the interactions between chromophores.

In general, the polarizability is directly related to the mobility of the charge carriers of the spacers; actually, it is easier to induce a dipole in a molecule whose electrons have a large enough mobility [5]. It suggests that the surface charge carriers of metallic nanoparticles can shield properly the dipole-dipole interactions between push-pull chromophores.

In a system with both of them, highly polarizable spacers with a negligible permanent dipole and chromophores with large permanent dipoles, the field due to the chromophores induce dipoles in the spacers; then besides the dipole-dipole interactions, the dipole-induced dipole ones take place in the system too. The dipole-induced dipole coupling can occur, turning more difficult the dipole-dipole aggregation of the chromophores. In consequence, materials doped with highly polarizable spacers increase the amount of non-self-coupled push-pull chromophores that they can host.

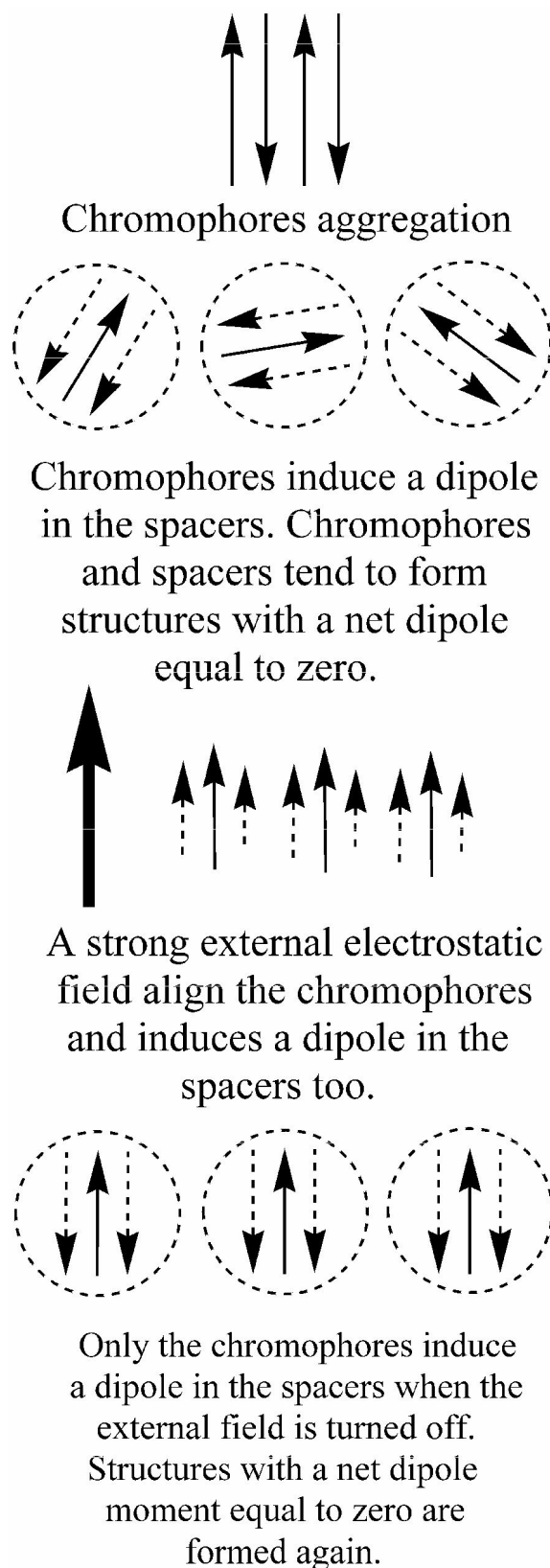


FIGURE 1. Scheme about how the polarization of the spacers helps to avoid the chromophores aggregation and to improve the chromophores alignment stability through an electrostatic shielding.

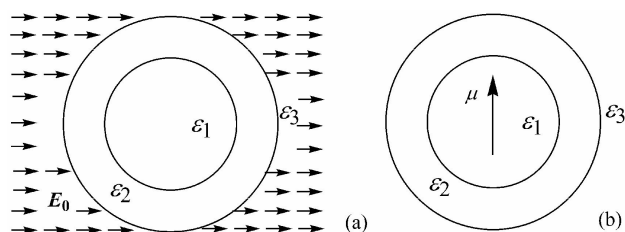


FIGURE 2. Schematic picture with the two cases considered from the Onsagers theory. (a) Polarizable shell inside a constant electric field. (b) Polarizable shell with a permanent dipole at its center.

This kind of highly polarizable spacer-chromophore system is attractive too for those materials in which their chromophores are oriented non-centrosymmetrically with the use of an external intense electrostatic field, because the external field also induces a dipole in the spacers, breaking any kind of zero dipolar moment formed in dipole-induced dipoles structures. Besides, when the external field is off, the chromophores are again the main responsible of the induced dipoles in the spacers, but now the induced dipoles are non-centrosymmetrically oriented too, which helps to maintain the particular orientation of the chromophores, *i.e.* it increases the stability of the system. The scheme in Fig. 1 exemplifies the situation.

Summarizing, the spacer works in two different ways: (a) as a physical spacer, increasing the distance between chromophores, and (b) as an electrostatic screen, shielding the electrostatic interactions between chromophores. In any case, the effect of a spacer should be stronger as its polarizability is larger.

In order to understand better the effect of the polarizable spacers on the chromophore-chromophore interactions we have taken into account an extension of the well known Onsagers theory for polarizable media [6].

We assume, as an approximation, that the molecular spacers modify in a continuous way the surrounding medium of each chromophore. We describe this surrounding medium by a spherical shell made mainly by spacers, with a  $\varepsilon_2$  dielectric constant, different from the dielectric constants corresponding to that of the outside shell medium made by the supporting matrix ( $\varepsilon_3$ ), and to that of the inside medium, where a chromophore can be hosted ( $\varepsilon_1$ ). It is reasonable to consider  $\varepsilon_1 \approx 1$  in those materials plenty of free volume cavities where chromophores can be hosted; that is the case of some polymeric or  $\text{SiO}_2$  sol- gel films [7,8].

Also, it is plausible to assume that the shell itself obeys the Clausius-Mossotti relation, *i.e.*, the dielectric constant of the shell is related to the density  $N$  and to the polarizability of the spacers by means of the equation:

$$\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} = \frac{N\alpha}{3}. \quad (2)$$

Two different situations are considered. In first place, as depicted in Fig. 2a, a system immersed in a constant electrostatic field; this situation is analogous to have a film immersed in an external electrostatic field. The field inside the

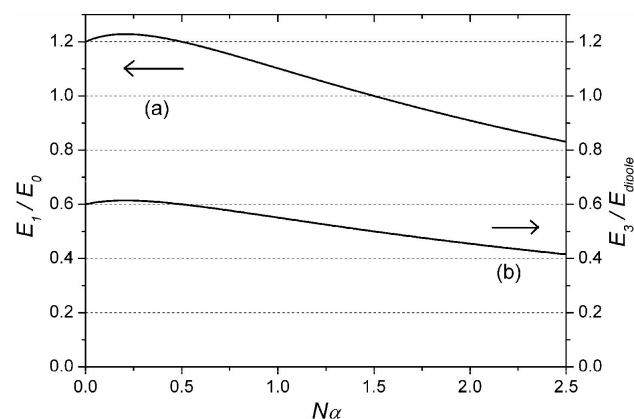


FIGURE 3. (a)  $E_1/E_0$  vs.  $N\alpha$  plot. (b)  $E_3/E_{\text{dipole}}$  vs.  $N\alpha$  plot.

shell is the field that a chromophore can experience; that field can eventually orient the chromophore in a particular direction. In second place, as depicted in Fig. 2b, a system without the influence of an external field, but with a dipole situated at the center of the shell; from this situation the field that another chromophore experiences outside the shell is determined.

After considering usual boundary conditions of continuity of the electrostatic potential and continuity of the electric displacement field between two adjacent media, following the procedure suggested by E. Riande *et al.*, [6] and Onsager [9], assuming that spacer molecules form a continuous shell that obeys Clausius-Mossotti relation and encloses an empty cavity, the results in terms of electric fields are: For the first case (a), inside the shell there is an electrostatic field with the same direction of the external field and with a constant magnitude everywhere. The ratio between the magnitudes of the electric field inside ( $E_1$ ) and outside ( $E_0$ ) the shell is given in the next equation

$$\frac{E_1}{E_0} = \frac{9\varepsilon_3(2N\alpha + 1)}{(2\varepsilon_3 + 2N\alpha + 1)(4N\alpha + 3)} \quad (3)$$

For the second case (b), the ratio between the magnitudes of the electrostatic field outside the shell  $E_3$ , when a permanent dipole is at the center of the shell, and the electrostatic field of the simple situation of a dipole in vacuum  $E_{\text{dipole}}$  is, everywhere:

$$\frac{E_3}{E_{\text{dipole}}} = \frac{9(2N\alpha + 1)}{(2\varepsilon_3 + 2N\alpha + 1)(4N\alpha + 3)}. \quad (4)$$

A plot of Eqs. (3) and (4) are shown in Fig. 3. In the case (a), the plot compares, as a function of  $N\alpha$ , the electric field magnitude in the region inside the polarizable shell (system with spacers) with respect to the electric field magnitude in the same region but without a polarizable shell, *i.e.* when  $\varepsilon_2=1$  (system without spacers).

In case (b), the comparison is done between the magnitude of the electric field produced outside the polarizable shell by the dipole (system with spacers), and the magnitude

of the electric field produced by the dipole when it is in vacuum, *i.e.*  $\epsilon_1 = \epsilon_2 = \epsilon_3 = 1$  (system without spacers).

Note that the plots are not 1 at  $N\alpha$  equal to zero, because at  $N\alpha$  equal to zero the equations still consider two different regions: supporting matrix and vacuum.

In Eq. (3) there are not spatial variables, it means that a dipole inside the shell experiences a spatially constant field, with the same direction of the external one; and for few  $N\alpha$  values, the field is even larger in magnitude. As the polarizability of the spacers and/or their concentration increase, the magnitude of the field inside the shell diminishes.

On the other hand, the field due to a fixed dipole inside the shell is always lower outside, with respect to the field produced by the dipole in the absence of the spacers ( $E_3/E_{\text{dipole}} < 1$ ). This field decreases its magnitude as the number of spacers and/or their polarizability increase.

All this means that spacers with large enough polarizabilities and negligible permanent dipole moments, in an appropriate concentration inside a material which hosts chromophores (SiO<sub>2</sub> is the hosting material in this work), decrease the dipole-dipole interactions between neighbor chromophores, but they still allow the molecular orientation by means of an external electric field. From this point of view, these spacers increase the stability of those materials which require a particular orientation of their chromophores.

This spherical shell model is a simplification of the real situation, but it clarifies the processes behind the influence that polarizable spacers exert on dipole-dipole chromophores interactions, even if the model is based on the assumption of a macroscopic, continuous and isotropic behavior of the media, which obeys the Clausius-Mossotti relation. In real materials there is a discrete ratio between the number of chromophores and the number of spacers.

Thus, highly polarizable nanoparticles, like silver nanoparticles, are good candidates to work well as molecular spacers.

### 3. Experimental details

In order to study how metallic nanoparticles influence push-pull chromophores aggregation in a real system, hybrid SiO<sub>2</sub> films doped with both, push-pull chromophores and silver nanoparticles, were synthesized. As stated in the previous section, we do not expect a strong aggregation of the push-pull molecules when the concentration and the polarizability of the spacers are high enough.

The formation of silver nanoparticles and their influence on the aggregation process was studied by UV-vis optical absorption spectroscopy as a function of the concentration of the chromophores in the films.

The UV-vis measurements were performed on each film, just after their deposition, using a JASCO V-570 spectrophotometer in transmission mode.

Hybrid organic-inorganic SiO<sub>2</sub> films were synthesized by sol-gel method. All the films were deposited on soda lime substrates by spin-coating at 1000 rpm for 30 seconds.

### 4. Materials synthesis

All the reactants were purchased from Aldrich.

2-{Ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino}-ethanol (also known as Disperse Red 1 or DR1) was used as a reference of push-pull chromophores with large dipolar moment (8.7 D).

Three different sol-gel precursors were used during the preparation of the hybrid matrix of the film, they are: Tetraethoxysilane (TEOS), (2-Glycidyloxypropyl)trimethoxysilane (GPTMS) and [3-(2-Aminoethylamino) Propyl]trimethoxysilane (AEAPTMS).

The synthesis was carried out in several steps. First, GPTMS and TEOS were prehydrolyzed by mixing GPTMS, TEOS, water and methanol (MeOH) in a [TEOS:GPTMS:H<sub>2</sub>O:MeOH] molar ratio equal to 1:2.33:6.66:18.33. GPTMS and TEOS are stirred together for 10 minutes at room temperature, and then water was added dropwise, followed by methanol. This solution was magnetically stirred for 10 minutes; finally, it was refluxed for 4 hours at 80°C. The final sol is named GT, and it has a theoretical silicon concentration of 2.08 moles/L.

In other flask, 5  $\mu$ l of AEAPTMS were added to 0.13 mg of silver nitrate (AgNO<sub>3</sub>) dissolved in 800  $\mu$ l of Methoxyethanol, and agitated ultrasonically during 15 minutes (some samples were made without AgNO<sub>3</sub>). Then, DR1 was added and stirred magnetically at room temperature during 15 minutes. At last, 30.3  $\mu$ l of GT were added. Everything is stirred magnetically during 30 minutes at 40°C.

The DR1 molecules are added in the next quantities: 0, 1.6, 5.0, 10.0 and 15.0 mg, corresponding to 0%, 5%, 15%, 30% and 45% molar of the push-pull chromophores with respect to the total theoretical silicon concentration in the material.

The AEAPTMS works in two different ways: (a) as a reducing agent, converting silver ions into metallic silver, and (b) forming organic bonds with the GPTMS.

### 5. Results and discussion

Through UV-vis spectra it is possible to detect the presence of free electrons on the surface of silver nanoparticles as well as the state of aggregation of push-pull chromophores, as reported in several works [10-14].

The UV-vis spectrum of a system with silver nanoparticles shows a plasmon resonance peak around 410 nm. In Fig. 4 there is a normalized UV-vis spectrum of the hybrid SiO<sub>2</sub> films made without DR1. The spectrum shows a plasmon resonance peak, evidence of the presence of silver nanoparticles in our samples. The spectrum was fitted using of a modified Gans theory [14], in order to know the main properties of the silver nanoparticles in our samples. Through the fitting it is possible to say that the samples have silver nanoparticles

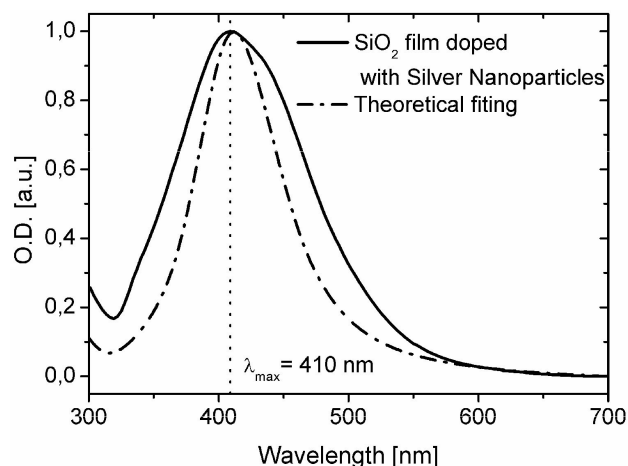


FIGURE 4. Normalized UV-vis spectrum of  $\text{SiO}_2$  films doped with silver nanoparticles. The dotted line is a modified Gans fitting to the spectrum.

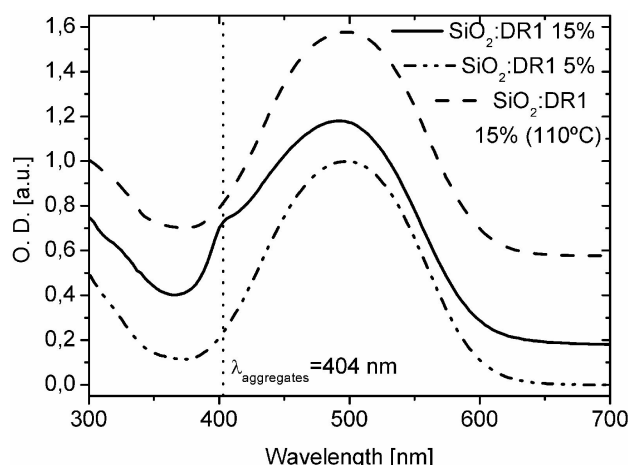


FIGURE 5. Normalized UV-vis spectra of  $\text{SiO}_2$  films doped with two different concentrations of DR1, but without silver nanoparticles. The normalization factor is the maximum value of each spectrum. For clarity, some spectra are vertically shifted.

which are not monodispersed, approximately 4.06 nm in diameter, with a 0.88 axial ratio, and they are surrounded by an effective local refractive index equal to 1.68.

On the other hand, the UV-vis spectrum of samples prepared without  $\text{AgNO}_3$  and low DR1 concentrations consists of a main band due to the electronic transitions of the DR1 double conjugated bonds system, superimposed to a baseline due to the matrix of the films. Their UV-vis spectrum can be taken as a reference of a system of DR1 molecules with negligible aggregation. Actually, the samples with low chromophores concentration are not affected by aggregation, due to the large distance among the chromophores inside a homogeneous film. In this way the electrostatic interactions among permanent dipoles become almost negligible, which is straightforward understandable from the fact that dipole-dipole forces between two molecules vary inversely as the 3rd power of the distance between the molecules [15]. Figure 5 shows the normalized spectrum of a film with a low

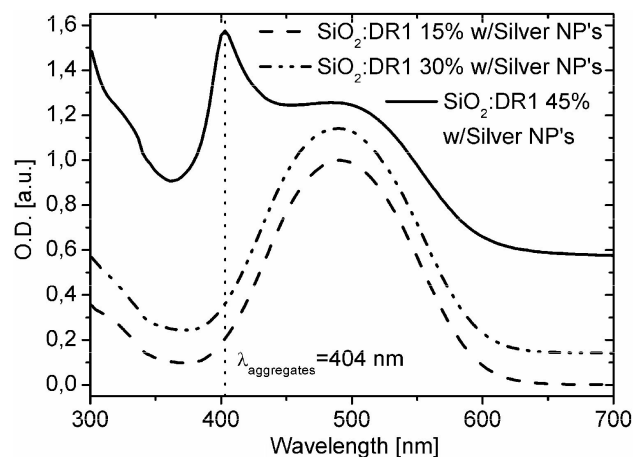


FIGURE 6. Normalized UV-vis spectra of  $\text{SiO}_2$  films doped with silver nanoparticles and three different concentrations of DR1. The normalization factor is the maximum value of each spectrum. For clarity, some spectra are vertically shifted.

amount of chromophores: only 5% molar of DR1 with respect to the silicon in the matrix. In this case the spectrum is centered at 496 nm.

The other normalized spectra of Fig. 5 correspond to films without silver nanoparticles too, but with a larger amount of DR1: 15% molar with respect to the silicon content. One of them was measured at room temperature; it shows an additional peak at 404 nm, because DR1 molecules form H-aggregates in the films [10]. The other one was measured in-situ at 110°C; it does not show the peak at 404 nm, because at 110°C the chromophores have enough mobility to break the aggregates.

It is clear that the peak at 404 nm is due to chromophores aggregation: when the DR1 concentration is low, that peak does not appear; when the DR1 concentration is higher that peak is present; if the sample is heated, the DR1 aggregates are broken and the peak at 404 nm disappears [16].

In Fig. 6 there are the normalized UV-vis spectra, taken at room temperature, of the films doped with a constant concentration of silver nanoparticles and several DR1 concentrations: 15%, 30% and 45% molar with respect to the silicon content. The spectra of the films with 15% and 30% of DR1 do not exhibit a peak at 404 nm, but the spectrum of the film with 45% of DR1 shows a clear aggregation peak at 404 nm. The effect of the silver nanoparticles is evident: they allow to increase the amount of non-aggregated DR1 molecules in  $\text{SiO}_2$  sol-gel films, because the aggregation of chromophores takes place at larger concentrations of DR1 molecules than those at which takes place in films without silver nanoparticles. It is only at larger concentrations than 30% of DR1 that chromophores aggregation appears.

The H-aggregates peak at 404 nm should not be confused with the plasmon resonance peak at 410 nm, this last peak does not appear in Fig. 6 because it is very small with respect to the height of the DR1 main band. It makes sense that the DR1 main band covers to the small plasmon peak, since the

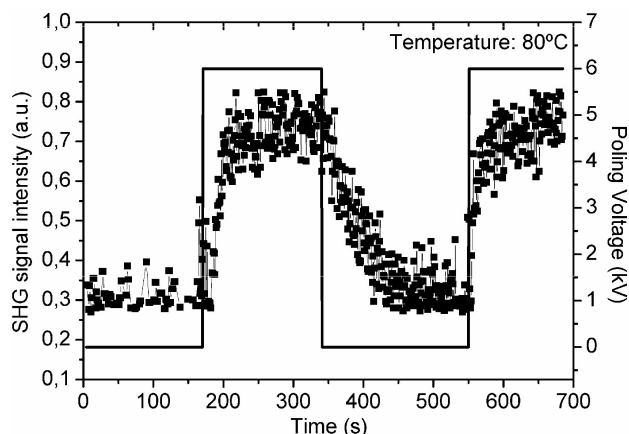


FIGURE 7. Second Harmonic Generation Intensity vs. Time plot, for films with 30% of DR1 at 80°C. The dots correspond to the SHG measurements. The continuous line corresponds to the Poling Voltage.

DR1 molecules are in more quantity inside the films, as the AgNO<sub>3</sub>:DR1 molar ratios of the samples suggest. The AgNO<sub>3</sub>:DR1 molar ratios are 1:20.8, 1:41.6 and 1:62.4 for DR1 concentrations of 15%, 30% and 45% respectively.

It is clear that the concentration ratio between push-pull chromophores and metallic nanoparticles plays an important role in the aggregation of the chromophores. For larger quantities of highly polarizable spacers the chromophores aggregation becomes more difficult to occur.

As Fig. 3 shows, it is not expected that the silver nanoparticles of the samples block completely any external electrostatic field. Thus an appropriate external electrostatic field could make the dipolar chromophores inside the samples rearrange in a non-centrosymmetric way. In order to confirm it and to confirm the potential use of these films in second order nonlinear optical applications, the films with 30% of DR1 and silver nanoparticles were subjected to a Corona poling process.

During the Corona poling process an intense external electrostatic field is applied on the films. The orientation of the molecules as function of the poling time was followed by Second Harmonic Generation (SHG) measurements. The

Corona poling set-up and the Second Harmonic Generation set-up are described elsewhere [17]. For this work the Corona voltage was 6 kV, the temperature was 80°C, and the incident angle of the fundamental beam of light was 40°. The results are shown in Fig. 7.

From Fig. 7 it is possible to see that the nanoparticles do not avoid the chromophores orientation neither the film Second Harmonic Generation. From Fig. 7 also it is recognizable the recovery of the chromophores orientation after their loss of orientation by thermal agitation.

A quantitative comparison between the Second Harmonic Generation intensities of the films with and without silver nanoparticles, as well as the temporal stability of the poled films are still in progress, the results will be discussed in a future work.

## 6. Conclusions

The molecular spacers avoid the dipole-dipole interactions between chromophores with high dipolar moments. Those interactions are screened better as the concentration of the spacer and/or its polarizability increase. This kind of electrostatic screening avoids the formation of aggregates in the sol-gel films, which is expected to increase their optical quality. The spectroscopic results on the formation of chromophore aggregates in the films are in agreement with the dependence on the concentration and polarizability of the spacers proposed by the theory. A great improvement in the optical quality of sol-gel films devoted to second-order non-linear applications could be possible by the incorporation of an appropriate amount of metallic nanoparticles as molecular spacers.

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