Nonlinear solid-state filter based on photochromism induced by 2-photon absorption in a dye-doped sol-gel

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ABSTRACT

There is much interest in enhancement of the absorbance performance of nonlinear absorber solid-state filters. In this work we present an advanced reversible nonlinear filter based on a dye-doped sol-gel matrix. The absorbance enhancement was achieved by using a combination of two absorption mechanisms in the same molecule; a photochromic absorption which is induced by 2-photon absorption (2PA). The 2PA serves as the trigger for initiating the photochromism through Förster-resonance-energy-transfer (FRET) between the fluorescent donor and the photochromic acceptor. We synthesized a new bifunctional-chromophore that incorporated a carbazole-derived 2PA fluorescent donor and a chromene-derived photochromic acceptor, covalently linked together in a single molecule by a ~6 Å carboxyl group or oxygen bridge. The bifunctional-chromophore was doped in an inorganic-organic hybrid matrix prepared by the fast-sol-gel process. These materials solidify without shrinkage or formation of cracks and present promising properties as optical matrices for smart filters. The dye-doped sol-gel disc presents high transparency in the visible region ("colorless"), which under UV-irradiation (one-photon absorption in the photochromic part of the molecule), transforms into a strongly absorbing filter ("dark colored"), due to the conversion of the photochromic moiety to its "open" absorbing form. We have demonstrated that this ring-opening can also be induced by visible-light (620 nm) using the 2PA carbazole-derived moiety of the molecule. We have studied the fabrication routes and optical performance of these filters. We present studies of the 2PA mechanism of the carbazole derivative, FRET efficiency of the combined-molecule as well as in solutions of the individual moieties, and reversible dynamics of the photochromic moiety.

Keywords

2-photon absorption (2PA), sol-gel, nonlinear solid-state filter, photochromism, Förster-resonance-energy-transfer (FRET), fluorescent donor, acceptor, inorganic-organic hybrid, bifunctional-chromophore, optical matrices.

1. INTRODUCTION

Nonlinear solid-state filters are devices, which can be highly useful in protection of optical sensors in advanced optical systems by controlling the exposed light intensity[1]. However in order to be suitable for use in such optical systems (e.g. observation, navigation, fire control and reconnaissance systems) these filters should comply with strict optical requirements on one hand and also offer significant performance on the other hand. New organic materials possess promising performances as nonlinear optical materials and the common way to dope organic molecules is to incorporate

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them in different host materials such as organic polymers. Matrices based on organic materials are usually not suitable as opto-electronic devices due to limitations in optical quality and durability. In contrast, ceramic glassy materials are a favored choice for fabrication of opto-electronic devices. Ceramic materials have several intrinsic advantages over polymers, such as high temperature durability, resistance to chemical attack, exceptional toughness and some ceramics possess excellent optical properties (e.g. SiO_2, TiO_2, Al_2O_3, and ZrO_2). The drawback of ceramics as matrices for incorporation of organic chromophores is that classical ceramic fabrication methods use high temperature which is not suitable for organic molecules. The sol-gel technology allows fabrication of optical glassy monoliths with desired dopants. There are many routes for fabrication of sol-gel monoliths. The sol-gel process is a chemical route to produce glassy based materials at low temperature[2-5]. Two main advantages of the sol-gel process are (1) the ability to incorporate in the sol-gel matrix various organic or inorganic functional additives and (2) the ability to produce versatile final configurations such as monolith/bulk glasses, thin films/coatings, nanoparticles and fibers. In addition the chemical and physical properties of the final product can be controlled during the process and properties such as porosity, density and specific linear and non-linear optical properties can be tailored. Therefore the sol-gel process can be treated as a "tool kit" which allows fabrication of a variety of monoliths differing in porosity and ingredients. Sol-gel technology offers the ability to dope an extended variety of additives, such as ceramic oxides, metal ions, inorganic compounds, metallic particles, quantum dots, organic dyes, and bio-molecules such as enzymes. Doping can be done in two different phases in the sol-gel monolith: as part of the network of the monolith or as encapsulation in the pores. Additional options can be in the interface. The main routes for doping are: mixing the dopants in the initial precursor solution, mixing the dopants with hydrolyzed sol before gelation, impregnation of dopant into the dried gel from solution or vapor state. For optical applications it is required that the homogeneity of the obtained samples will be on the order of several nanometers, otherwise there will be significant scattering effects. Recently, we developed a new class of sol-gel materials, which are made of a combination of silica alkoxides and organic modified silica alkoxides with final low organic content (<30%). The fabrication process named fast sol-gel (FSG)[6] provides materials without shrinkage and cracks that can be used as optical devices and as adhesive materials, and can be doped with varied dopants such as carbon nanotubes and organic dyes[7-8].

Many materials and molecules were already studied as candidate dopants for a nonlinear optical (NLO) filter, such as inorganic nano-crystals[9,10], quantum dots[11,12], carbon based nano-particles[13,14], and organic dyes presenting 2-photon absorbing (2PA) or excited state absorbing (ESA) properties[15-17]. The desire requirements from NLO filters are to transmit light with lower irradiance input and become strong absorbing at higher irradiance. The expected performance from the NLO filter is to present a broadband nonlinear absorption which can be use for optical limiting applications in the visible spectrum. Already have been proposed many mechanisms such as 2PA[18,19], ESA[20,21], reverse saturable absorption (RSA)[22,23], nonlinear scattering[24,25], etc. Most of the materials were studied in solution or suspension state[9,11,-14,17-20] and the minority in solid matrix, mainly in organic polymer [21,22,26-29] and lately also in sol-gel based matrices[30-32]. Unfortunately most of these extensive studies did not result in NLO filters which appropriate for optical limiting applications in real optical systems. From the point of the functional NLO material, in most cases, the obtained optical limiting was not sufficient for practical applications, and from the matrices point of view a filter contain solvent is not desire and organic matrices are lack due to limitations in optical quality and durability.

Since the performance obtained when using only one of these nonlinear mechanisms may not meet the application requirements, due to insufficient nonlinearity of the materials. Previously, it was suggested to use additional mechanisms in order to enhance the performance[33]. This can be achieved by two separate mechanisms, such as has been demonstrated in multiphasic nanoporous glass[34] or two coupled mechanisms via resonance energy transfer (RET)[35,36]. Previously, a 2PA mechanism coupled via RET with reverse saturable absorption (RSA) has been demonstrated in solution[35]. In this paper we suggest a mechanism to enhance 2PA performance by coupling it with photochromic material where all doped in a solid-state matrix based on sol-gel technology with improve optical properties. In this case, the 2PA serves as the trigger for initiating the photochromism through a Förster-resonance-energy-transfer (FRET) between the fluorescent donor and the photochromic acceptor. FRET is a mechanism describing the energy transfer from an excited donor to an acceptor through nonradiative dipole-dipole coupling[37,38]. Photochromism, defined as a reversible transformation within a unimolecular species, induced in one or both directions by electromagnetic radiation[39], attracts considerable interest owing to the potential use of this phenomenon in various applications. Among such applications, the development of optical data storage materials[40] optical limiting[41] and manipulating supramolecular self-assemblies[42] should be mentioned. Using two-photon absorption (2PA) instead of one-photon absorption for inducing photochromic transformations offers further advantages and opens new possibilities in data recording and biomedical applications[43].

Most of the known organic photochromes have strong and broadband linear absorption in the visible spectrum at open form, but they usually possess very small 2PA cross section values[44] and the target of rendering them large 2PA strengths is complicated. An alternative approach involves resonance energy transfer (RET) from a 2PA capable fluorophore as a donor and a photochrome as an acceptor. Previously, we demonstrated that a solution mixture of a fluorophore and a spiroxazine-derived photochrome (as an acceptor) absorbs two photons and exhibits RET[33,45]. But in order to achieve process with decent FRET efficiency required short distance between the donor and the acceptor molecules, called Förster radius[33]. For a molecule mixture in solution or solid matrix achieving Förster radius required very high concentration (> 10^{-2} M), which is usually above the maximal dissolved concentration. In this work we present a new bifunctional-chromophore (incorporates 2PA donor and a photochromic acceptor linked together by a ~6 Å bridge) possessing pohotochromic behavior triggered by 2PA mechanism and incorporate it in a solid state matrix prepared by the sol-gel process. The concept of the combination of the two mechanisms is presented in Figure 1; a long wavelength excitation is absorbed by 2-photon absorbing (2PA) chromophore, which acts as donor, and transfers its energy via a resonance energy transfer (RET) to a photochromic (PC) material, which acts as the acceptor. The PC material, which initially was in its "closed ring" (colorless) form, is converted to the "open ring" (colored) form, leading to an enhanced absorption at the long wavelength.

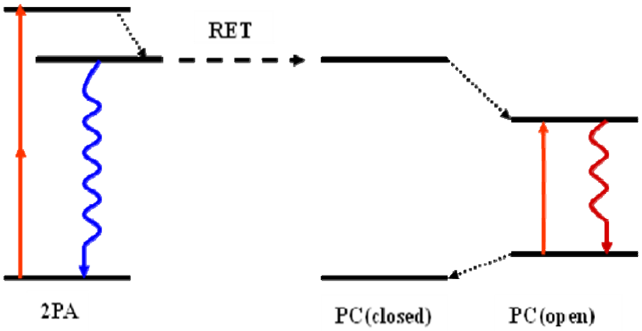

Figure 1: The concept of the combination of the two mechanisms, schematic energy level diagram of resonance energy transfer (RET) between 2-photon absorber (2PA), the donor, and photochromic (PC) material, the acceptor. The PC converts from "closed" (colorless) form to "open" form (colored).

2. EXPERIMENTAL

We synthesized a new class of bifunctional-chromophore that incorporates a carbazole-derived 2PA fluorescent donor and a chromene-derived photochromic acceptor, covalently linked together in a single molecule by a ~6 Å carboxyl group bridge. The detailed synthesis and spectroscopic properties of these compounds in solution are presented elsewhere[46]. Specifically, two photochromic derivatives were studied; one presenting a color change from "colorless" to "red" (designated as PC1) and the second one from "colorless" to "dark purple" (designated as PC3). To each of them a carbazole-derived 2PA fluorescent donor moiety was attached via the carboxyl group or oxygen bridge. Figure 2 presents the molecular structures of the bifunctional-chromophores and of a model photochromes without the 2PA moiety for PC1 derivative (2a & 2b) and for PC3 derivative (2c & 2d) together with the carbazole-derived 2PA derivative (2e). Figure 3 presents the equilibrium between the "closed-ring" form and the "open-ring" form, obtained after UV irradiation, for both photochromic derivatives, PC1b (3a) and PC3b (3b).

The bifunctional-chromophores were doped in an inorganic-organic hybrid matrix prepared by the fast-sol-gel process. These materials solidify without shrinkage or formation of cracks and present promising properties as optical matrices for smart filters. A detailed description of the fast sol-gel method can be found in ref 6. Briefly, sol-gel precursors (alkoxides and organically modified alkoxides) are mixed and undergo hydrolysis and condensation. The precursors used for the FSG reaction were tetramethylorthosilicate (TMOS), methyltrimethoxysilane (MTMS), 3-(methacryloxy)-propyltri-methoxysilane (MATMS), and 0.005 N HCl as the catalyst. The precursors (98% purity) and HCl (0.1 N) were purchased from Sigma–Aldrich, and tetrahydrofuran (THF) high performance liquid chromatography (HPLC)-grade were purchased from BioLab Ltd. All chemicals were used as purchased. The fast sol-gel reaction is performed at a temperature of about 100ºC under time-varying pressure conditions (from several atmospheres to vacuum). In this way a viscous sol-gel resin is quickly produced which, after a fast and simple curing process, leads to the final glass-like product. Avoiding the use of a common solvent as well as the continual removal of the liquid phase formed during the reaction, significantly decreases the processing time and eliminates the contraction volume and fracture formation. The obtained viscous sol-gel resin can be either immediately solidified or dilute by a solvent, such as THF, for later use. The FSG technique allows reproducible preparation of materials with well controlled properties. By changing the ratio of the precursors or the organic residues, the end product can be varied between a silicone rubber and a silica glass. Thus, the mechanical and optical properties of an FSG resin can be custom designed for required specifications between these two extremes. In the current work, we transform the sol-gel matrix to a more hydrophobic environment in order to increase the solubility and stability of the dopant chromophores in the sol-gel matrix. This issue regarding photochromic materials in sol-gel matrices was discussed previously by Levi et. al.[47]. Therefore, an alkoxide acrylic precursor (3-methacryloxypropyl-trimethoxysilane (MAPTMS), a precursor with one organic and three inorganic polymerizable tails, was added. In this case, the molar ratio of the precursors (TMOS:MTMS:MAPTMS) was 1:5.6:0.4. The chromophores PC1 and PC3 were dissolved in THF solution at concentrations ranging from 10^{-5} – 10^{-3} M. Then, the chromophores-THF solution was added to the diluted sol-gel solution in THF, in ratio 1:1. In order to achieve solid discs the THF was evaporated almost to completion for a few minutes in open air. Afterward, the obtained viscous gel was poured into a 35-mm diameter Petri dish, and covered with a lid. Bubbles were removed under slow evacuation conditions in pumped desiccators and then the resin was cured at room temperature for 48 hr and final curing at 65 ºC for 24 hr. We obtained optically clear (and colorless) solid disk without shrinkage and cracks.

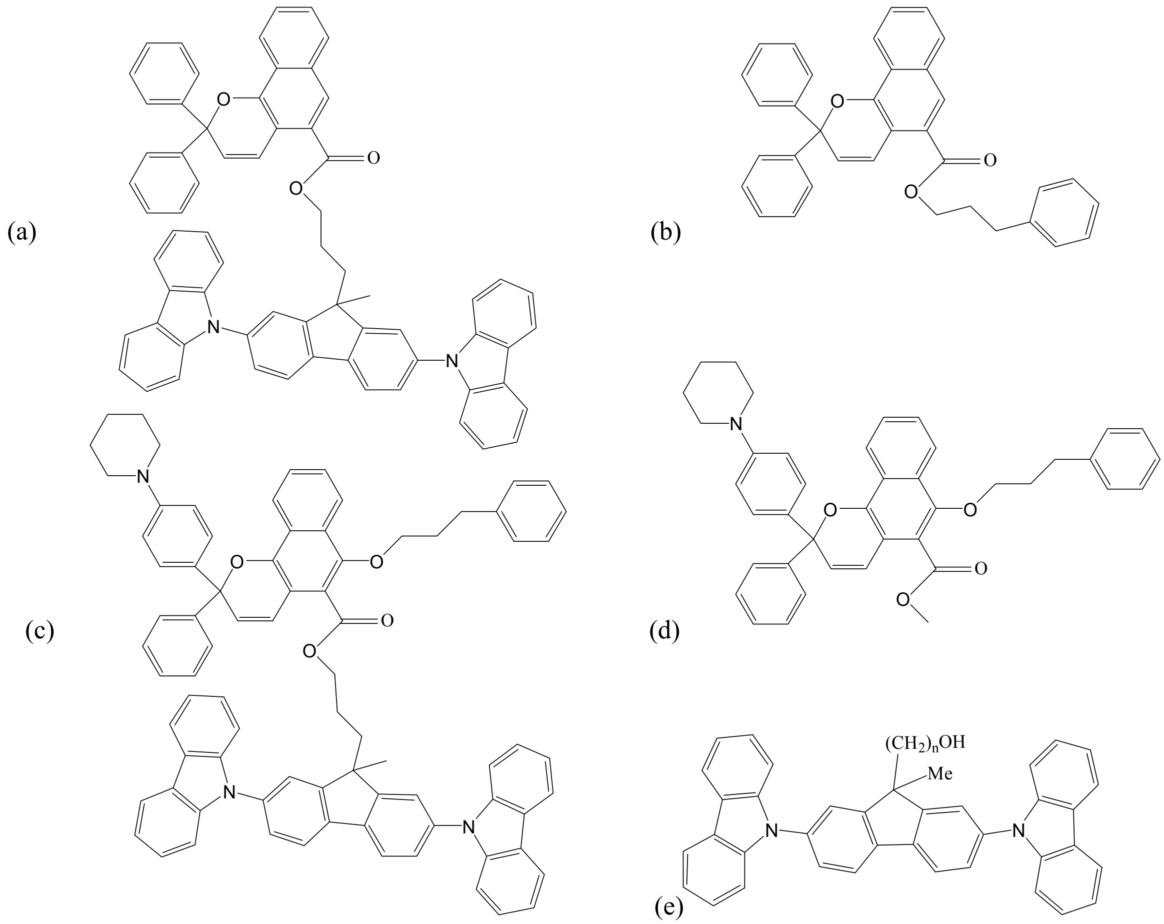

Figure 2: Molecular structures of the photochromes; chromene (naphthopyran)-derived photochrome PC1 the bifunctional-chromophore (a) and the model photochrome without the 2PA moiety (b), chromene (naphthopyran)-derived photochrome PC3 the bifunctional-chromophore (c) and the model photochrome without the 2PA moiety (d), and the 2PA chromophore carbazole-derived, 2,7-bis(carbazolyl)fluorine (e).

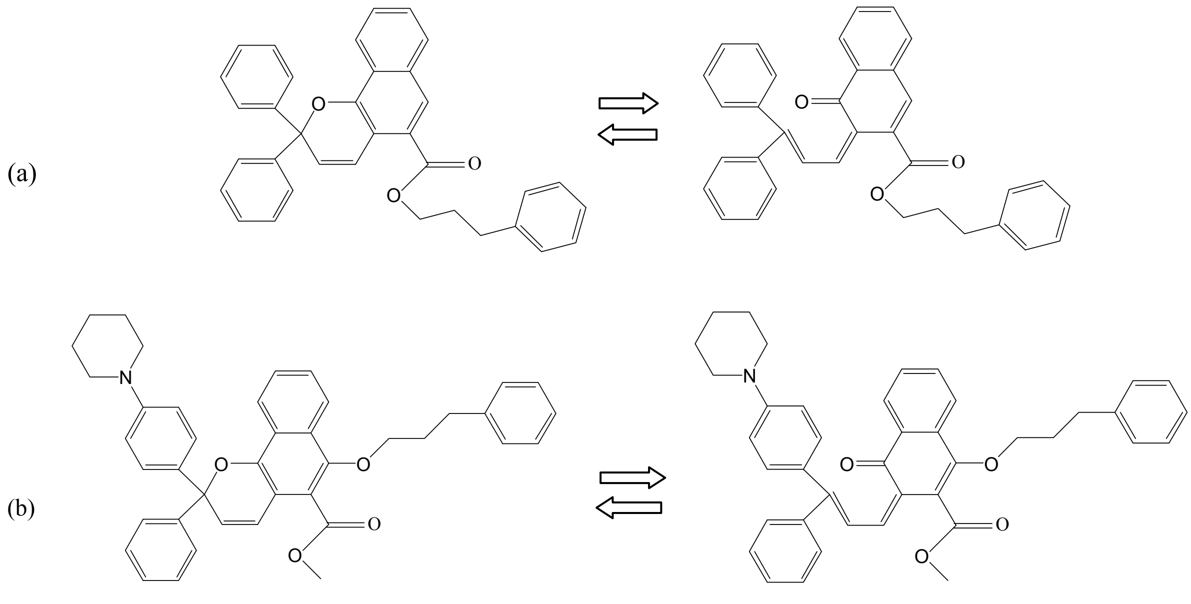

Figure 3: Molecular structures of the equilibrium between the "closed-ring" form and the "open-ring" form, obtained after UV irradiation, for the chromene (naphthopyran)-derived photochrome PC1 (a) and PC3 (b).

The photochromic behavior of the doped sol-gel discs was tested under UV-irradiation from a Blue Wave 200 UV lamp manufactured by Dymax (with 7 W/cm^2 at the UV region). The spectral properties were measured using Ocean Optics fiber spectrometer, QE-65000 in the spectral range 200 -1000 nm using a DT-MINI-2-GS Ocean Optics lamp as a source. The FRET studies were done using 325 nm CW laser for one photon excitation and by using femtosecond pulse laser at 620 nm for 2-photons excitation.

3. RESULTS AND DISCUTION

Sol-gel disc samples (radius of 3.5 cm and thickness of 1 mm) doped with the photochromic derivatives PC1 or PC3 (concentration of ~1 x 10^{-3} M) present under UV light illumination a significant high contrast reversible change from a colorless disk ("closed" form) to a “Red” or "Purple" ("open-ring" form) disc, for PC1 and PC3 respectively, seen in Figure 4 (a & c). The characteristic absorption spectrum of the reversible change is presented in Figure 4 (b & d). The absorption was measured before and after illumination with the UV lamp. The obtained spectra under this illumination intensity exhibit molar absorption extinction coefficients of ~15,000 M^{-1}cm^{-1} at 460 nm ("Red") for PC1 and ~15,000 M^{-1}cm^{-1} at 520 nm ("Purple") for PC3. The open photochrome decays spontaneously back to the closed form in a few minutes. The doped sol-gel glass discs present reversible color changes for many cycles.

The concept of photochromism induced by 2PA and FRET was demonstrated with a sol-gel disc doped with PC1a derivative, a bifunctional-chromophore. A femtosecond laser pulse at 620 nm was used for excitation of the 2PA carbazole derivative moiety in the bifunctional-chromophore. The 2PA was followed by a FRET mechanism from the carbazole moiety which serves as the donor to the chromene photochrome moiety which serves as acceptor. The resulting process was a color change in the sol-gel glass disc in the size of the laser beam from "colorless" to "red" due to the ring-opening in the photochromic moiety which occurs during the femtosecond pulse used. The sol-gel glass disc, with PC1 concentration of 0.6 x 10^{-3} M/L and thickness 1 mm, present a color change (can be seen in figure 5a), were the colored area is in the size of the excited beam laser (circled). In this case the decay to the initial state (fading of the color) takes about 4 minutes as result of a thermally reversible process (seen in 5b). The obtained spectrum of the "open-ring" derivative peaks at 460 nm and its decay with time is also presented (Fig. 5c).

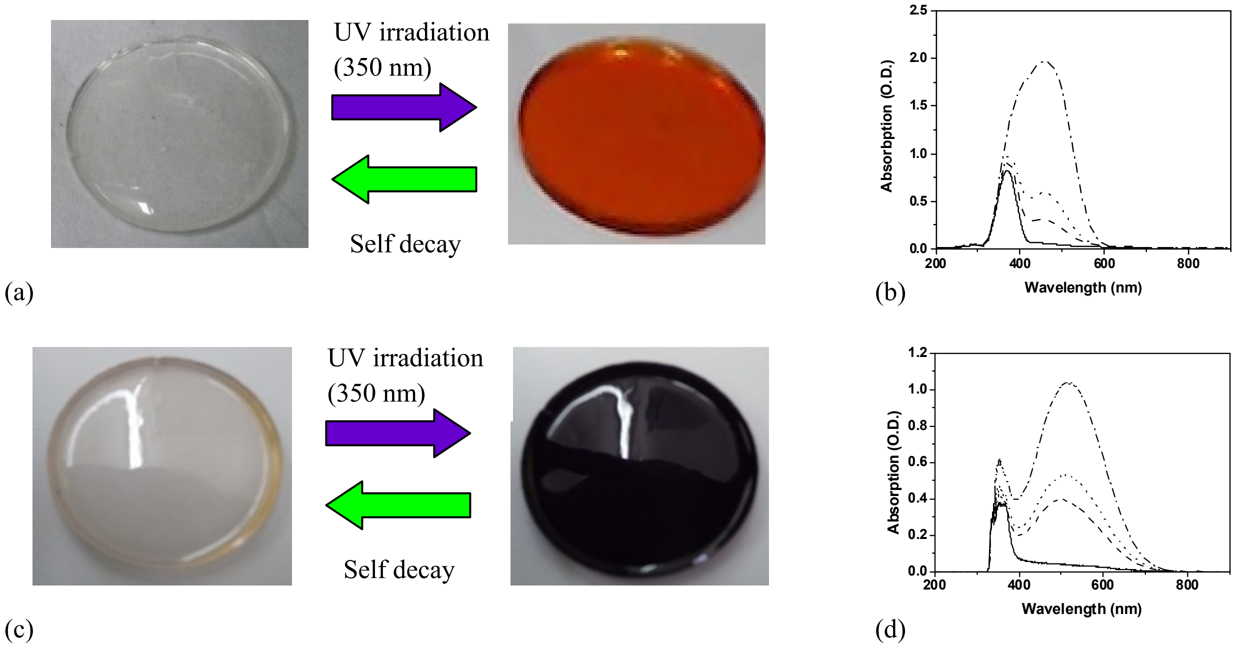

Figure 4: Photos of the reversible color change of sol-gel disc samples (radius of 3.5 cm and thickness of ~1 mm) doped with photochromic derivatives PC1 (a) or PC3 (c) before and after UV-irradiation. Characteristic absorption spectra of the reversible color change for PC1 (b) and PC3 are shown in (b) and (d) respectively ("closed form" full line curve "open form" dash-dot curve). After UV-irradiation PC1 derivative presents a "Red" color with absorption peak at 460 nm, PC3 presents a "dark Purple" color with absorption peak at 520 nm.

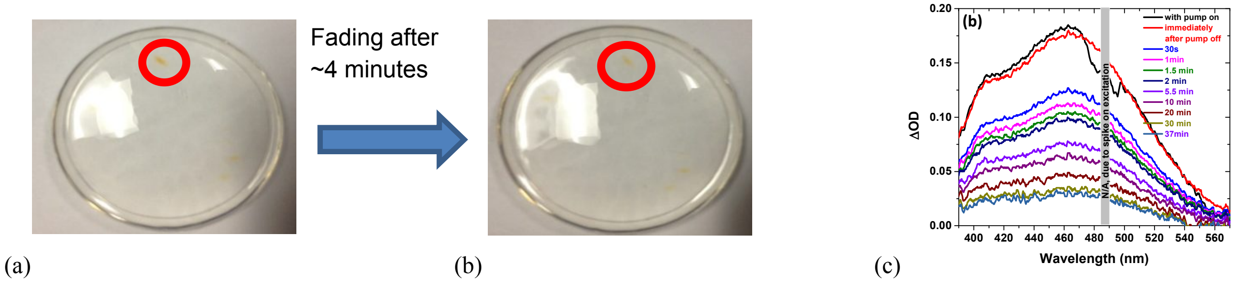

Figure 5: (a) Photo of the reversible color change of sol-gel disc samples due to excitation by a femtosecond pulsed laser at 620 nm resulting in photochromism induced by 2PA-FRET mechanism in the laser beam area (circled). (b) The color fades in ~4 minutes as a result of a thermally reversible process. (c) The obtained spectrum of the "open-ring" derivative peaking at 460 nm and its decay with time.

To determine the FRET efficiency of the bifunctional-chromophore within the sol-gel matrix we compared between sample doped with the bifunctional-chromophore, PC1a, to a sample doped with a mixture of the two chromophores, the 2PA donor and the model photochrome without the 2PA moiety, PC1b, the acceptor[48]. In order to extract the FRET efficiency a 2-level model was developed[49] in which the closed- and open- molecular forms are treated as ground and excited states (shown in the inset of Fig. 6a). In this case the total process efficiency, Φ_{total}, can be expressed by the following equation:

$$(1) \qquad \Phi_{total} = A_{Donor} * \Phi_{FRET} * \Phi_{PC} + A_{Acceptor} * \Phi_{PC}$$

Where A_{Donor} and $A_{Acceptor}$ are the partial absorption by the donor and the acceptor, Φ_{FRET} is the net FRET efficiency and Φ_{PC} is the net photochromic efficiency (closed to open form). In this way the total process efficiency was extracted from the data of the sample of bifunctional-chromophore in sol-gel, while the partial photochromic efficiency was extracted from the data of the sample with mixed chromophores in sol-gel. The 2-level model gives 5% total efficiency from the fit for the bifunctional-chromophore in sol-gel, and 15% photochromic efficiency from the fit for the of the individual donor and photochrome mixture in sol-gel, which results in 23% FRET efficiency. Fig. 6b shows the accumulative opening time dynamics of the bifunctional-chromophore in sol-gel excited from complete closed-form with different excitation intensity, I_0, where ΔOD reaches steady state around 300s. Applying similar efficiencies obtained from steady state fit, the 2-level model also gives reasonable theoretical predictions regarding the opening photokinetic measurements, and the small discrepancy between the curves is possibly due to the fact that the 2-level model only allows for one effective time constant considered in this multi-exponential reversing process.

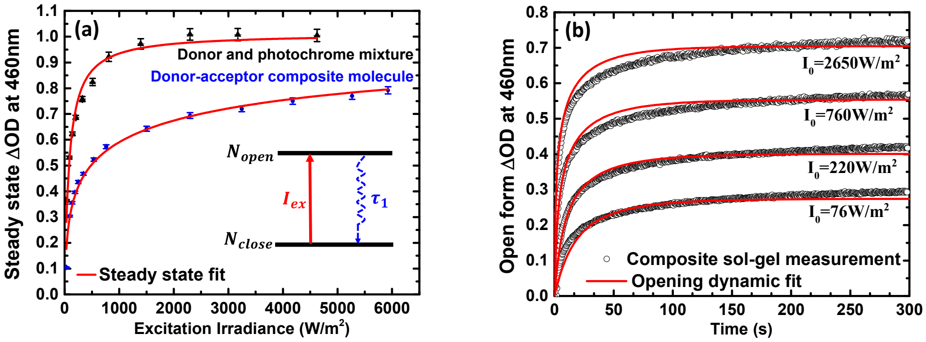

Figure 6: (a) The dependence of the steady state ΔOD (460nm) on excitation irradiance I_0 (325nm) for the bifunctional-chromophore and the mixture doped sol-gel, fit by a 2-level model (inset) to obtain total efficiency (from the bifunctional-chromophore in sol-gel) and the photochrome efficiency (from the mixture sol-gel). (b) The opening photokinetic measurements for the composite sol-gel with different excitation irradiances are fit by the 2-level model.

4. CONCLUSION

We present a route for fabrication of nonlinear optical solid-state filter composed of chromophores doped in a sol-gel matrix with improved optical properties. In order to enhance the nonlinear optical absorption performance two absorption mechanisms were coupled together via resonance energy transfer (RET); 2-photon absorption (2PA) and photochromism. We demonstrate photochromism induced by 2PA followed by Förster-resonance-energy-transfer (FRET) for a new bifunctional-chromophore doped in a sol-gel matrix. Under excitation with a visible laser beam (620 nm) a reversible color change from colorless to red is obtained with absorption spectrum peaked at 460 nm due to an "open-ring" of the photochromic moiety. By applying a 2-level model analysis, the FRET efficiency (23%) can be estimated from the simple UV-excitation (1PA) based photokinetic measurements.

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