Two-Photon Photochromism of an Organic Material for Holographic Recording

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We report the two-photon-induced photoisomerization of 3-[1-(1,2-dimethyl-1H-indol-3-yl)-ethylidene]-4-isopropylidene-dihydrofuran-2,5-dione (**1**), a photochromic compound with $\lambda_{max} = 385$ nm, using 775-nm femtosecond pulsed laser irradiation. The resulting photoisomer had $\lambda_{max} = 582$ nm. The kinetic rate constant for the two-photon-induced electrocyclic isomerization reaction was measured at two different intensities (two different powers), showing a quadratic dependence with respect to the pump intensity. Results of pump−probe solution phase experiments and guest/host polymer thin film interferometric imaging studies are reported. A two-photon absorption molecular cross section $\sigma 2 = 10.3 \times 10^{-48}$ cm^4·s/photon was measured using Z-scan, further supporting a two-photon-induced isomerization process. Two-photon-induced interferometric recording in a fulgide-containing polymer film was demonstrated.

Introduction

The field of two-photon organic photochemistry is in its infancy, not unlike the field of single-photon organic photochemistry 50 years ago. Two-photon transitions can be described by two different mechanistic types. For nonpolar molecules with a low-lying, strongly absorbing state near the virtual level, only excited states that are forbidden by single-photon selection dipole rules can be populated via two-photon absorption (Type 1 in Figure 1).[1] The probability that this low-lying state can contribute to the virtual state is predicted by Heisenberg's uncertainty principle, with a virtual state lifetime approximated as $h/(4\pi\Delta E)$, where h is Planck's constant and ΔE is the energy difference between the virtual and actual states. Using this equation, it is predicted that an allowed state can contribute to the formation of the virtual state for time $t_{virtual}$, which is equal to about $h/(4\pi\Delta E)$ with the transition probability proportional to $\Delta\mu^2$. For example, a lifetime of ca. 0.3 fs is estimated for a state separation of 0.1 eV. Two-photon absorptivity, δ, is expressed in Goeppert−Mayer units (GM), with 1 GM $= 1 \times 10^{-50}$ cm^4 s molecule^{-1} photon^{-1}. Molecules that undergo strong 2PA via the Type 1 process have two-photon absorptivities up to 10 GM.[2]

In contrast, strong 2PA can occur in polar molecules by a different mechanism (Type 2 in Figure 1) in which a large change in dipole moment ($\Delta\mu$ > 10 D) occurs upon excitation of the ground to an excited state.[1] Single-photon allowed states can then be accessed via 2PA, and the transition probability scales with $\Delta\mu^2$. In this case, both the ground and excited states can participate in the formation of the virtual state, enhancing 2PA. In polar molecules with large $\Delta\mu$ between the ground and excited states, δ values in excess of 100 GM have been reported.[1,3−5]

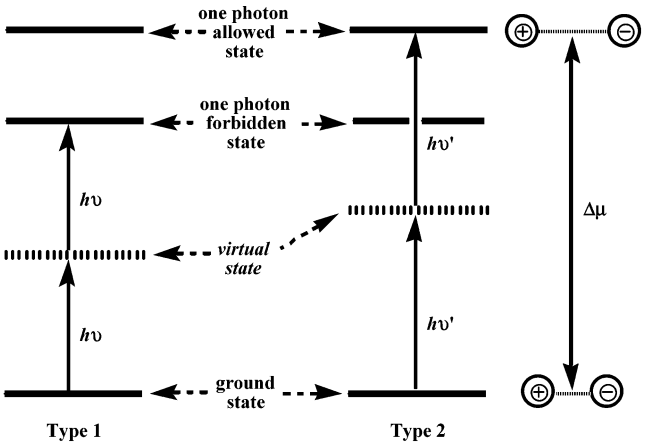

Figure 1. "Simultaneous" two-photon absorption processes (Types 1 and 2).

The quadratic, or nonlinear, dependence of two-photon absorption on the intensity of the incident light

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has substantial implications. For example, in a medium containing one-photon absorbing chromophores, significant absorption occurs all along the path of a focused beam of suitable wavelength light. This can lead to excitation outside the focal volume. In a two-photon process, negligible absorption occurs except in the immediate vicinity of the focal volume of a light beam of appropriate energy. This allows spatial resolution about the beam axis as well as radially, which circumvents out-of-focus absorption and is the principal reason for two-photon fluorescence imaging.[6] Particular molecules can undergo upconverted fluorescence through nonresonant two-photon absorption using near-IR radiation, resulting in an energy emission greater than that of the individual photons involved (upconversion). The use of a longer wavelength excitation source for fluorescence emission affords advantages not feasible using conventional UV or visible fluorescence techniques, for example, deeper penetration of the excitation beam and reduction of photobleaching.

Rentzepis and co-workers reported two-photon-induced photochromism of spiropyran derivatives at 1064 nm.[7,8] Analogous to single-photon absorption facilitated isomerization, the spiropyran underwent ring-opening isomerization to the zwitterionic colored merocyanine isomer. The merocyanine isomer underwent 2PA at 1064 nm, resulting in upconverted fluorescence. Spiropyrans are known to undergo photobleaching and photodegradation upon prolonged exposure; hence, they are not suitable for long-term use. Nonetheless, an intriguing model for 3-D optical storage memory was proposed.

Like many spiropyrans, spirooxazine and fulgide-type compounds are known to undergo photoisomerization from a colorless to highly colored isomer.[9] Unlike the spiropyrans, the thermally and photochemically stable spirooxazine and fulgide-type compounds have been reported which underwent numerous single-photon photochemical isomerization (color) and reversion cycles without significant degradation,[10] though stability is highly structure-dependent.[8,11] Optical data recording potentials as high as 100 million bits/cm^2 have been reported for fulgide-type materials. To enhance photochemical stability, fluorinated indolylfulgides have been investigated.[12] In an effort to investigate the potential of indolylfulgides for two-photon holographic imaging and information storage, indolylfulgide **1** (λ_{max} = 385 nm) was chosen for study, particularly because its single-photon photochromic behavior is well established (Figure 2).[13]

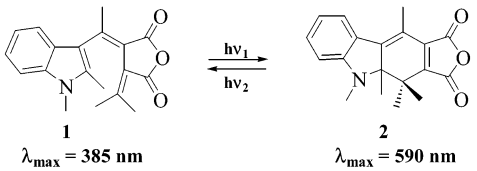

Figure 2. Photoisomerization of indolylfulgide **1**.

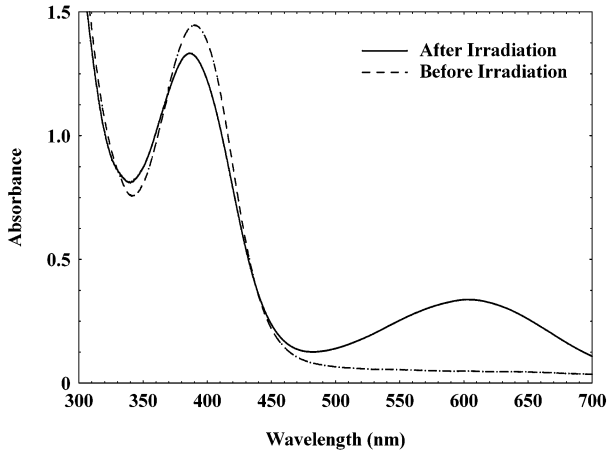

Figure 3. Absorption spectra of **1** before and after exposure to 350-nm UV irradiation.

Experimental Section

Materials. The indolylfulgide **1** was prepared, starting from 1,2-dimethylindole, following literature procedures.[13−16] Preparation of the phosphorylated poly(VBC-*co*-MMA) used for the formation of the polymer film was described previously, consisting of a mole ratio of diethyl vinylbenzylphosphonate to MMA of 1:3 in the polymer.[17] Solvents were purchased as HPLC or spectrophotometric grade from Sigma-Aldrich and used as received.

General Procedures. *Single- and Two-Photon-Induced Isomerization Studies of* **1** *in Solution*. For the single-photon-induced isomerization, indolylfulgide **1** was dissolved in toluene and transferred to a quartz cuvette (10-mm path length). The sample was purged with N_2 for 10 min and irradiated with a broadband UV light source (300−400 nm) in a Rayonet photoreactor. The photoisomerization reaction progress was monitored by UV−visible absorbance spectra on a Varian Carey 3 spectrophotometer.

Two-photon-induced isomerization was performed with a pump−probe experimental setup. A toluene solution of **1** (4.53×10^{-3} M) was deaerated by purging with N_2 for about 10 min prior to transfer into a 12-μL quartz cuvette. The cuvette had 1-mm-wide clear windows on three sides, one facing the femtosecond laser pump beam with the probe beam incident on an adjacent side. The detector (Ocean Optics fiber optic spectrometer detector) was placed behind the sample to monitor changes in transmittance with and without pump beam exposure. The femtosecond source used was a CPA-2001 laser system from Clark-MXR. Femtosecond pulses from a frequency-doubled erbium-doped fiber ring oscillator are stretched to about 200 ps, then passed through a Ti:Sapphire regenerative amplifier, and compressed down to 160 fs. The peak energy of a single pulse (centered at λ = 775 nm) was 137 nJ at a 1-kHz repetition rate. This yields a peak irradiance, I_0, of 60 GW/cm^2. The beam was focused to a spot size w_0 = 39.7 μm (HW1/e^{2}M) into a 1-mm cell thickness. The concentration of **1** in toluene was 4.53×10^{-3} M. The probe beam was provided by a tungsten−halogen lamp (440−800 nm) and cutoff filter. The irradiation was carried out at different exposure times. A kinetic study of the isomerization

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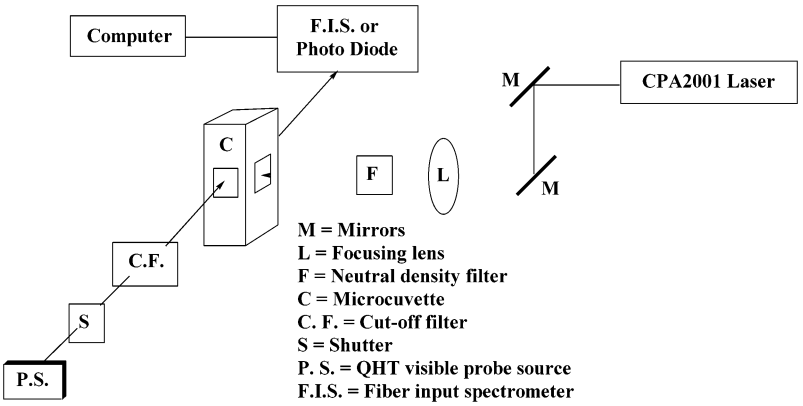

Figure 4. Optical system for pump−probe photoisomerization and kinetics experiment.

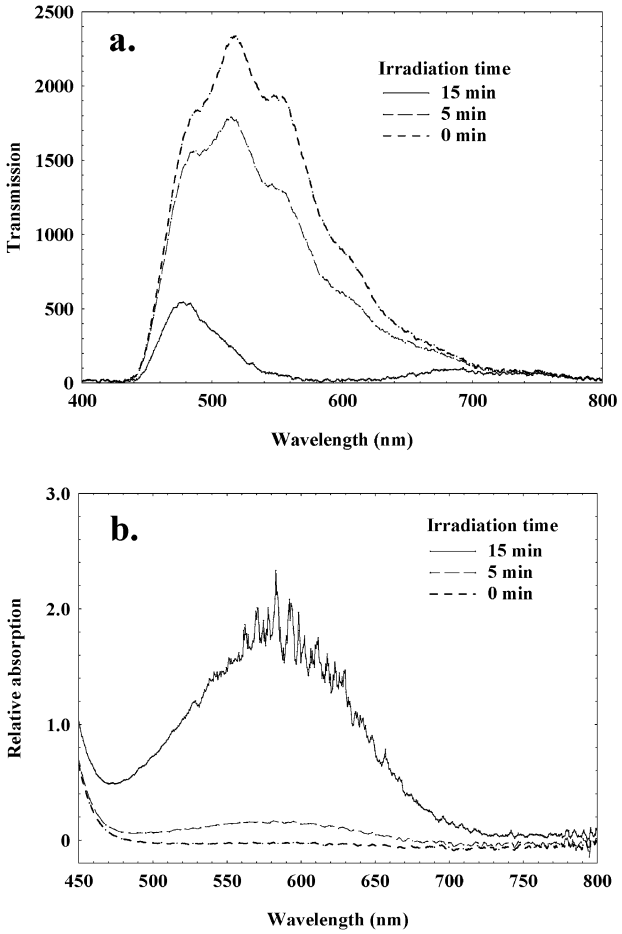

Figure 5. Transmission spectra (a) transformed into the absorption spectra (b) as a function of time for the two-photon-induced photoisomerization of fulgide **1** using a 775-nm femtosecond pump beam.

process utilized the same experimental setup, except the detector was changed to a GaAsP diode detector with the probe chopped at a frequency of 1 kHz such that 1000 ± 1 pulses arrived at the sample in a 1-s time interval.

Two-Dimensional Holographic Recording. A copolymer of a phosphorylated poly(VBC-*co*-MMA) (21 wt %) was first dissolved in *p*-dioxane, to which **1** (1 wt % relative to the polymer) was added. The polymer solution was purged with N_2 for 10 min followed by ultrasonic degassing. A thin film (5 μm) was prepared by spin coating onto a glass substrate (2000 rpm, 40 s) with a photoresist spin coater from Headway Research Inc. The film was carefully kept in the dark to avoid any external irradiation exposure. This polymer was chosen due to its excellent solubility, ability of the polymer to solubilize organic

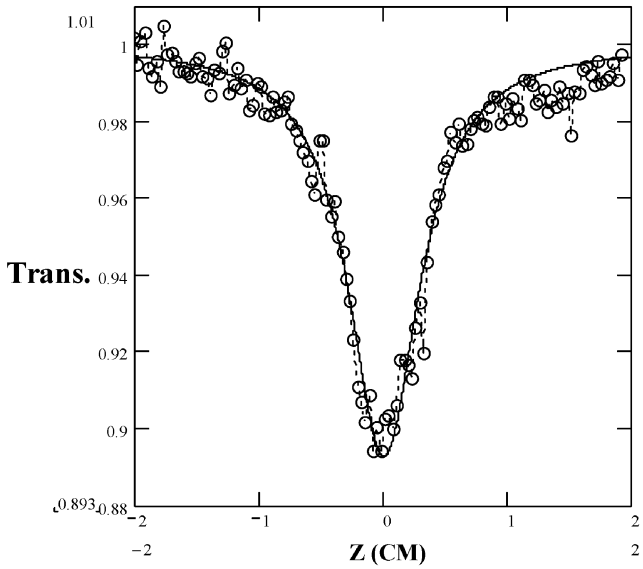

Figure 6. Normalized transmittance of a 4.53 mM toluene solution of fulgide **1** vs the cell position around the focal plane. The total energy/pulse (centered at λ = 775 nm) is 137 nJ at a 1-kHz repetition rate. The beam was focused to a spot size w_0 = 39.7 μm (HW1/e^{2}M) into a 1-mm cell thickness. The solid curve is given by eq 1 with a fitting parameter of β = 0.11 cm/GW.

dyes without phase separation, and our extensive experience using this in thin film applications. Dry 1,4-dioxane was found to be a good solvent for both spin coating and solution casting films of this polymer.

To demonstrate two-dimensional (2-D) interferometric recording, an experiment was performed using a Mach−Zender interferometer with the same laser system described above. The beam size was 3-mm diameter and the peak energy was 120 μJ (peak irradiance, I_0 = 11 GW/cm^2). Using a CE, CV-252 video camera with pixel size (12 × 12 μm), the interference pattern at the sample plane obtained by the spatial and temporal overlap of two pulses was monitored. The beam was directed onto the copolymer thin film doped with **1** to induce photoisomerization. An Olympus BH-2 optical microscope equipped with a CCD camera and SPOT software was used to examine and capture the resultant polymeric image and measure image dimensions.

Results and Discussion

A toluene solution of indolylfulgide **1** in a 12-μL quartz cuvette was irradiated with UV light in a Rayonet photoreactor (350-nm broadband bulbs). Changes in the UV−visible absorption spectrum were recorded

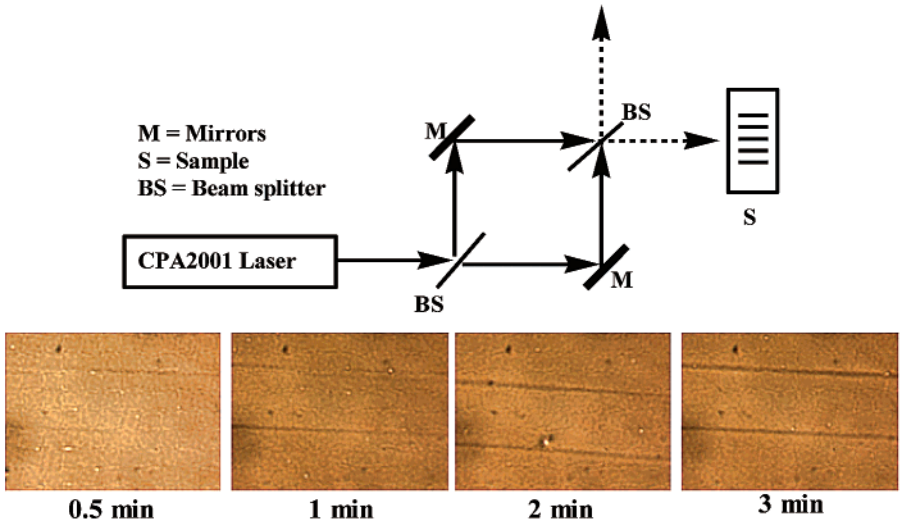

Figure 7. Schematic of a Mach−Zender interferometer (upper) for 2-D recording via two-photon photochromism (beam splitters are 50:50 at 45°, laser exposure time = 0.5−3 min, output beam angle = 2°). Dark lines in image (lower) result from high-intensity bright fringe-induced photoisomerization of fulgide **1** in a polymeric film (13-μm line width and 155-μm line spacing).

as a function of irradiation exposure to monitor the isomerization process (Figure 3). The absorption at 590 nm reached its maximum after 1 min, with a concomitant decrease at 385 nm, and was accompanied by a solution color change from pale yellow to deep blue. Upon irradiation with visible light (400−800 nm), the absorption at 590 nm decreased, while the absorption at 385 nm increased, resulting in the solution reverting back to the original yellow color. These results indicated **1** underwent reversible electrocyclic ring closure to form the ring-closed isomer **2** upon irradiation with UV light. Formation of the six-membered ring isomer allowed the anhydride and the indole ring to become coplanar, extending the conjugation and delocalization of the π system, which was monitored at 590 nm. The process can be reversed by irradiation with visible light, where the closed form **2** undergoes presumed conrotatory motion, to generate the opened form isomer **1**.

To demonstrate the possibility of two-photon-induced photochromism for **1**, determination of the kinetics of femtosecond near-IR (775 nm) photoisomerization was performed using a pump−probe experimental setup (Figure 4) to verify the two-photon-induced nature of the transformation. The laser beam was focused into a 12-μL quartz microcuvette. A shuttered tungsten halogen lamp (400−800 nm) was used as the probe to monitor the reaction, with a cutoff filter (<440 nm) placed between the probe and the sample to eliminate linear absorption effects of the isomerization process.

The transmission spectrum displaying the formation of the fulgide photoisomer **2** was monitored as a function of time (Figure 5a) and transformed into the absorption spectrum (Figure 5b). The appearance of the absorption band at 590 nm, coincident with the single-photon photoisomerization process, demonstrated that two-photon-induced isomerization of **1** into **2** occurred. A control experiment was performed with the 775-nm pump beam blocked to examine possible linear absorption effects from the probe beam. No absorption was observed in the visible region during 30 min of irradiation by the probe beam, eliminating the possibility of single-photon-induced photoisomerization.

To support a two-photon-induced process, a kinetic study was performed to investigate the dependence of the photoisomerization rate on incident intensity. Plots of absorbance at 585 nm (log I_0/I) versus time (s) were linear for the formation of the longer wavelength absorbing ring-closed photoisomer **2**. The photoisomerization rate constants thus obtained were $2.53 \times 10^{-3} \pm 0.3 \times 10^{-3}$ s $^{-1}$ and $6.99 \times 10^{-3} \pm 0.5 \times 10^{-3}$ s^{-1} at average powers of 3.5 and 7.0 mW, respectively. The rate constants exhibited a near-quadratic dependency as a function of incident intensity for the photoisomerization of **1** to **2** with the 775-nm femtosecond pump beam, supportive of a two-photon-induced process.

To further confirm that the two-photon absorption (2PA) process is responsible for the isomerization of **1**, the two-photon coefficient of **1** was measured with an open aperture Z-scan.[18] According to Sheik-Bahae et al.,[18] assuming Gaussian input beam and using a Gaussian decomposition method, the transmittance can be described as

$$T(z) = \sum_m \frac{-q_0(z)^m}{(m+1)^{3/2}} \qquad (1)$$

where $q_0(z)$ is in ratio with the two-photon absorption coefficient (β), peak irradiance (I_0), effective length (L_{eff}), position of the cell (z), and diffraction length of the beam (z_0).

$$q_0(z) = \frac{\beta I_0 L_{\text{eff}}}{\left(1 + \left(\frac{z}{z_0}\right)^2\right)} \qquad (2)$$

The transmittance vs cell position is shown in Figure 6. Experimental data (open circles) show that indeed this compound exhibited 2PA at this wavelength. The theoretical fitting (solid line) using eq 1 corresponds to $\beta = 0.11$ cm/GW, yielding a 2PA molecular cross section $\sigma 2 = 10.3 \times 10^{-48}$ cm^4·s/photon. The high 2PA cross

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section that this compound exhibits at 775 nm, and its photochromic properties, makes fulgide **1** an interesting material for holographic applications.

To demonstrate two-dimensional (2-D) interferometric recording in a polymeric film, an experiment was performed using a Mach−Zender interferometer (Figure 7) and the same laser system described above. For this experiment, the beam was not focused into the sample. The beam sizes were 3-mm diameter and the total energy/pulse was 120 μJ (peak irradiance, $I_0 = 11$ GW/cm^2). Using a CE, CV-252 video camera (pixel size = 12 $\times$ 12 μm), the interference pattern was monitored at the sample plane obtained by the spatial and temporal overlap of two pulses. Photoinduced changes were observed in the region of high light intensity in a thin film of a poly(methyl methacrylate)/phosphorylated styrene copolymer composite doped with fulgide **1** on a glass substrate.

The micrographs in Figure 7 display the two-photon-induced reaction in the polymeric matrix with progressively longer exposure times. After 3-min of continuous irradiation, dark lines in the image can clearly be seen, resulting from the high-intensity bright fringe-induced photoisomerization of fulgide **1**. The angle between both beams was 2° to generate more lines over the sample. The distance between fringes was 155 μm, while the thickness of each fringe was 13 μm. The results demonstrate the possibility of using two-photon-induced photoisomerization of a fulgide for holographic recording in a polymeric medium.

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