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Transient Ring Opening and Closing of a Two-photon Photochromic Molecule Utilizing Energy Transfer

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Abstract: We have developed an efficient two-photon photochromic molecule by coupling a chromene with a donating 2PA chromophore via resonance energy transfer. The essential parameters of ring opening and closing are determined from transient absorption measurements.

OCIS codes: (190.4400) Nonlinear optics, materials; (190.7110) Ultrafast nonlinear optics; (190.4710) Optical nonlinearities in organic materials; (260.2160) Energy transfer;

1. Introduction

Photochromism of spiro-type compounds have received great interest for ultrafast photonic applications such as optical memory and switching [1]. The lower energy form usually contains a closed ring structure, which only absorbs in the ultraviolet (UV) spectral range. Upon UV irradiation, bond cleavage occurs between the sp^3 carbon and oxygen atoms resulting in an open form. This is followed by *cis-trans* isomerization, resulting in an extended conjugation of the π -electron system exhibiting a broadband visible absorption. The open form may thermally fade back to the initial transparent closed form, with an extremely long lifetime. This back-transfer process may also be induced by absorbing a visible photon, which is known as photochemically induced ring closure [2]. The photo-induced ring opening and closing processes are usually completed within a few tens of picoseconds, accompanied by multiple transient photoproducts [2]. Ring opening can also be initiated through simultaneous absorption of two visible photons. This two-photon absorption (2PA) induced photochromism has been applied to high-density 3D optical storage [3]. Here, we are interested in the use of two-photon photochromism to enhance nonlinear absorption (NLA). Activated by 2PA, the initial transparent closed form starts to linearly absorb at the same wavelength as the 2PA excitation due to ring opening, which adds extra NLA in addition 2PA. Therefore, two-photon photochromic molecule is a potential candidate for making visible optical limiters with a truly broadband absorption.

Most photochromes are not optimized to have large 2PA cross sections (i.e. $< 10 \text{ GM}$), making the 2PA induced photochromic transformation inefficient. To overcome this limitation, we have synthesized a novel bifunctional molecule (denoted PC-1 in Fig. 1c) by covalently linking a photochrome, 2H-benzo[h]chromene (2H-naphtho[1,2-b]pyran) (Fig. 1a), with a 2PA chromophore, 9,90-(9-(3-hydroxypropyl)-9-methyl-9H-fluorene-2,7-diyl)bis-9H-carbazole (Fig. 1b), via a 5-7 Å carboxyl bridge in an inter-orthogonal configuration [4]. Due to resonance energy transfer (RET) coupling between the 2PA donor and the photochromic acceptor, we observed $\sim 14 \times$ enhancement of the 2PA induced photochromic transformation compared to the pure photochrome. The linear absorption spectra of PC-1, 2PA donor and chromene dissolved in dichloromethane (DCM) are shown in Fig. 1d, where the relatively weaker absorption band at 370-400 nm and the stronger band between 300-370 nm originate from the photochromic moiety and 2PA donor, respectively. As a result of ring opening, a broadband absorption forms in the visible spectral range, i.e. 400-600 nm with a maximum at $\sim 460 \text{ nm}$. In earlier studies, we have confirmed the energy transfer from fluorescence measurements of the quantum yield, excitation spectra and anisotropy [5], and the thermal dynamics were measured by studying the accumulation of open-form populations of a dye-doped sol-gel matrix [6]. Here, we perform femtosecond pump-probe measurements to resolve the transient photoproducts with the quantum yields, reaction time constants and absorption cross sections.

Fig. 1. Molecular structures of (a) photochrome, (b) 2PA chromophore and (c) composite molecule PC-1; (d) the absorption spectra in DCM of closed- and open-form PC-1, 2PA chromophore and chromene.

2. Experiment and discussion

In this experiment, the transient ring opening is studied with both one- and two-photon excitation. The wavelength of one-photon excitation (Pump_{UV}) is 388 nm which only excites the photochromic moiety of PC-1. The two-photon excitation ($\text{Pump}_{2\text{PA}}$) is 620 nm, where the induced open-form absorption is negligible. To investigate photon induced ring closing, the excitation (Pump_{C}) is chosen at 510 nm within the open-form absorption band. The probe wavelength is 450 nm for all the experiments. By applying Pump_{C} after Pump_{UV} at the time delay when the molecule is not fully opened, ring closing dynamics of the intermediate open-form transients can be measured. To avoid the accumulation of the long-lived open form, we flow the PC-1 solution through a 1 mm thick spectroscopic cell, so that the material is replenished within the beam size for each laser shot. Here, the repetition rate is 1 kHz.

Fig. 2. Data (circles) and fits (lines) of transient absorption measurements of (a) one-photon ring-opening processes (inset shows measurements with two energies within 3 ps); (b) 2PA followed by RET ring-opening processes and (c) ring-closing photochromic reactions.

The measured normalized transmission of the probe upon one-photon opening is shown in Fig. 2a, where the magnitude of the signal scales linearly with the energy of Pump_{UV} . After the closed form is excited, it first relaxes from a higher electronic state to a vibrational state of a lower electronic state, resulting in an excited-state absorption (ESA) at ~ 500 fs. After overcoming the energy barrier, chemical bond cleavage between sp^3 carbon and oxygen occurs for the next few picoseconds, which leads to an intermediate open form (denoted conformer A), inheriting an orthogonal parental geometry with a smaller absorption at 450 nm compared to the initial ESA. Finally, the slowly increasing absorption in the next ~ 20 ps originates from the stabilization of open form by rotation of two equal Phenyl groups farther from the naphthalene moiety. This forms the metastable open form (denoted conformer B) with extended π -electron system indicating the completion of the ring-opening process. By numerically solving the time evolution of the population in each state, we have a unique set of parameters to fit the measured transient absorption dynamics, which yields a ring-opening quantum yield of $30 \pm 7\%$ and an absorption cross-section of $3.7 \times 10^{-17} \text{ cm}^2$ for conformer B. With $\text{Pump}_{2\text{PA}}$, PC-1 and 2PA chromophore solutions are measured under identical experimental conditions (see Fig. 2b), where they show the same signal at zero delay following the cross-correlation of $\text{Pump}_{2\text{PA}}$ and probe, which originates from the nondegenerate 2PA of the 2PA chromophore (donor) only. The fits give a 2PA cross-section of $\sim 103 \text{ GM}$. For the 2PA chromophore, the signal remaining at longer delays is attributed to the ESA induced by degenerate 2PA of the $\text{Pump}_{2\text{PA}}$ itself, which quadratically scales with the excitation energy. An ESA cross-section of $16 \times 10^{-17} \text{ cm}^2$ is determined, which is larger than that of conformer B. However, this long-lived ESA is not capable of remaining in PC-1, which instead exhibits a decay of absorption to a smaller value in ~ 8 ps. This maybe because coupling with the chromene via RET, the excited 2PA chromophore has another channel to relax to, initiating the ring-opening process as discussed above. Our analysis yields a RET efficiency of $76 \pm 10\%$, in agreement with the theoretical predictions considering a Förster radius of 0.7 nm. The ring closing dynamics are measured by applying Pump_{C} on conformer B solutions optically produced by illuminating the PC-1 solution reservoir with GaN LEDs emitted at 365 nm. As shown in Fig. 2c, the saturation of the open-form absorption occurs, accompanied by an intermediate closed form in ~ 1 ps, which results in ring-closing with an efficiency of $12 \pm 3\%$. In another closing experiment performed on a commercially available chromene, 3,3-Diphenyl-3H-naphtho[2,1-b]pyran, with open form produced by Pump_{UV} , we have observed that the conformer A may have a higher closing efficiency than conformer B. We thus provide insight into the 2PA-RET photochromic reaction schemes as well as the associated essential parameters for various photonic applications, e.g. optical limiting.

4. References

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