Förster Energy Transfer to a Spirooxazine Photochromic Molecule through One- and Two-Photon Absorption

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Abstract: Förster resonance energy transfer from a two-photon absorber to a photochromic spirooxazine are investigated by one- and two-photon absorption. Upon energy transfer, fluorescence of the donor is quenched while that of the photochromic is enhanced.

OCIS Codes: (160.4330) Nonlinear optical materials; (260.2160) Energy transfer

1. Introduction

Förster resonance energy transfer (FRET) [1], from an excited donor to an acceptor, through nonradiative dipole-dipole coupling, has many applications in optical sensors and switches [2,3], tracking dynamics of biomolecules [4]. Depending on the application and/or system to be studied, donor systems can be composed of simple organic dyes or inorganic quantum dots [5], or more complicated fluorescent proteins. The efficiency of FRET depends on several factors: (1) the spectral overlap between donor fluorescence and acceptor absorption; (2) the average distance between the donor and acceptor; and (3) the relative dipole orientation.

Photochromism is a reversible transformation between two forms of a molecule having different absorption spectra, In previous work we suggested the use of FRET from a two-photon absorbing dye to photochromic material in order to increase non-linear absorption [6]. In this work, the FRET between a two-photon absorbing dye (4,4'-bis(2,7-dicyclohexyl-9H-carbazol-9-yl)biphenyl) named M17, and a spirooxazine photochromic molecule (2-((1,3,3-trimethylspiro[indoline-2,3'-naphtho[2,1-b][1,4]oxazine]-5'-yl)methylene)malononitrile) referred to as SP01 is shown by one- and two-photon excitations. The open and closed form molecular structures of SP01 and the structure of M17 are shown in Fig. 1a, along with their linear absorption spectra and the fluorescence spectrum of M17 dissolved in dichloromethane (DCM) in Fig. 1b.

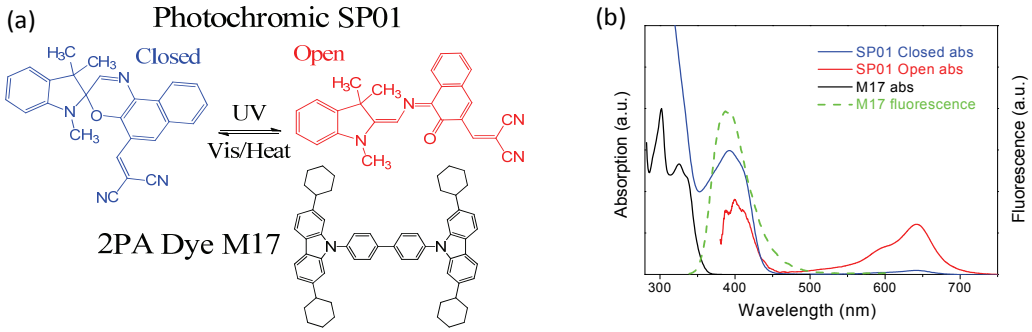

Figure 1. (a) Molecular structure of the open and closed forms of SP01 and M17, and (b) the linear absorption of the open and closed forms of SP01 and M17 along with the fluorescence spectrum of M17 in DCM.

Since M17 shows significantly larger two-photon absorption (2PA) cross sections, δ, compared to the photochromic molecule, a large quantum yield, and large spectral overlap of its emission with the closed form of SP01 (Fig. 1b), we expect these two molecules to show significant FRET.

2. Results and Discussion

Determining intra- and intermolecular spectroscopic properties and dynamics of a bimolecular system requires optical measurement techniques involving both time-resolved and steady-state measurements. Additional difficulty is encountered when one of the constituent molecules, in this case the photochromic acceptor SP01, has its own "bimolecular nature", an open and closed form, each with its own spectroscopic properties. Effectively, this becomes a tri-molecular system with both intra- and intermolecular properties. Our measurements utilize both

continuous and pulsed laser systems (femtosecond to nanosecond pulses) to quantify the many optical parameters needed to understand such systems. To measure the shape of the open form absorption of SPO1, the closed form SP01 is excited by a 400 nm continuous wave (CW) light emitting diode while probing with an absorption spectrophotometer. The opening dynamics have been measured using a femtosecond pump, white-light continuum probe (~150 fs FWHM at 1 kHz repetition rate) using a flow cell to avoid cumulative processes. As demonstrated in Fig.2a, at 1 ps after excitation, a broadband absorption from 450-900 nm is observed which is due to the intermediate forms of the photochromic molecule [7]. After ~20 ps the sample reaches its open form with a well defined absorption peak at 640 nm, consistent with the steady-state absorption spectrum in Fig. 1b. The closing time was measured by a single shot pump-probe using a ~4 ns pump at 355 nm and CW probe at 620 nm. The closing time was measured to be ~11 seconds.

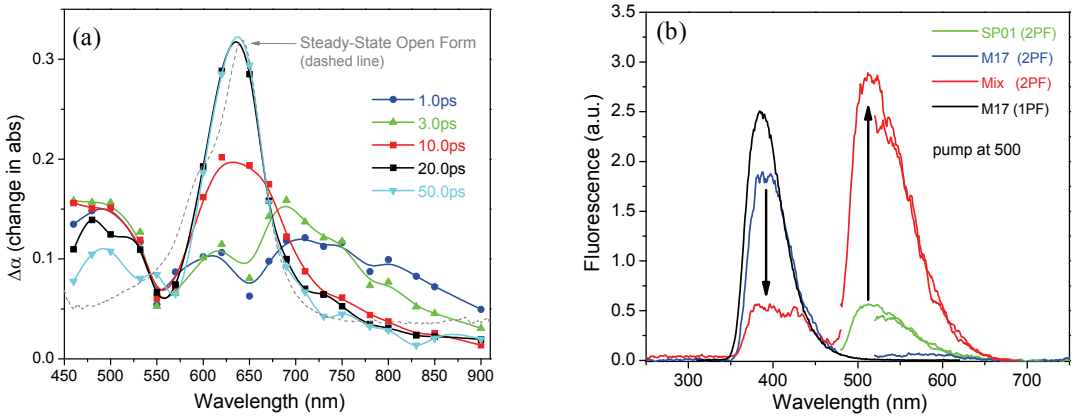

Figure 2. (a) Opening dynamics of SPO1 using a femtosecond pump at 390 nm and white-light continuum probe with a flow cell set-up, (b) two-photon excited fluorescence (pump at 500 nm) of SPO1, M17, and the mixture of both in DMC.

Two-photon excited fluorescence was used to investigate the presence of FRET between the two molecules. A mixture of SP01 and M17 is used with the same concentration of 2 mM, (for this concentration the FRET efficiency is calculated to be ~80 %). Figure 2b shows the experimental result with excitation at 500 nm, (where SP01-closed form and M17 show 2PA cross sections of ~20GM and ~1000GM respectively). The results show quenching of the fluorescence of M17 when mixed with SP01, while for the SP01 the fluorescence is enhanced. It is worth noting that the fluorescence observed from SP01 in this experiment is due to its closed form. No indication of two-photon absorption induced FRET leading to the open form is observed, but this could be due to the fact that the visible excitation leads to the closing of the open molecules [8]. We also observe quenching of M17 fluorescence for 1 photon excitation and 300nm.

3. Conclusions

We report observations of FRET from a two-photon absorber to a spiro-oxazine photochromic molecule via one- and two-photon excitations. The fluorescence quenching of the donor molecule (M17) in the presence of the acceptor (SP01) is an indication of FRET. In both experiments the donor showed quenching, which resulted in an increase of the closed form SP01 fluorescence under two-photon excitation.

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4. References

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