

Förster Resonance Energy Transfer within a Donor-Acceptor Composite Photochromic Molecule through One- and Two-Photon Absorption

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Abstract: FRET within a donor-acceptor composite photochromic molecule was investigated in a dye-doped sol-gel matrix using both 1 and 2-Photon absorption. The energy transfer efficiency was estimated from UV-excitation photokinetic measurements by applying a 2-level model.

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

1. Introduction

Organic photochromism refers to a thermally/photochemically reversible transformation within a unimolecular species, and is generally induced by electromagnetic radiation between two states having distinguishable absorption spectra [1]. It has been demonstrated that Förster resonance energy transfer (FRET) from an excited donating molecule (donor) to a photochromic accepting chromophore (acceptor) could also lead to photochromism through nonradiative dipole-dipole coupling [2-3]. In previous work, we synthesized a bifunctional composite photochromic molecule by incorporating a 2-photon absorbing (2PA) donor and a photochromic acceptor into a single molecule covalently linking them via a carboxyl group bridge, in order to enhance nonlinear absorption from 2PA-FRET induced photochromism for optical limiting application [3]. Strong evidence from the fluorescence measurements show that this donor-acceptor composite molecule allows FRET to occur in extremely low concentration solutions [3]. However, we encountered difficulties to determine the FRET efficiency, ϕ_{FRET} , and photokinetic properties of this composite molecule from simple UV-excitation (1PA) measurements on solutions, due to the following factors: (1) molecular diffusion in solution occurs in real time which limits the accumulation of the excited molecules; and (2) both donor and acceptor absorb UV excitation photons resulting in two separate photochromic transformation processes either through FRET from the donor with overall efficiency ϕ_{total} or through direct excitation of the acceptor with photochromism efficiency ϕ_{PC} . In this work, we doped the photochromic dyes into sol-gel materials, so the molecules are localized in the sol-gel matrix to overcome the diffusion problem. The sol-gel matrix used is a glassy inorganic-organic hybrid matrix prepared by the fast sol-gel process, which are solidified without shrinkage or formation of cracks and present promising transparency and thermal stability properties for optical applications [4]. The FRET efficiency within the bifunctional composite molecule was determined by using a 2-level theoretical model which was developed to estimate ϕ_{FRET} from the UV-excited accumulative photokinetic measurements.

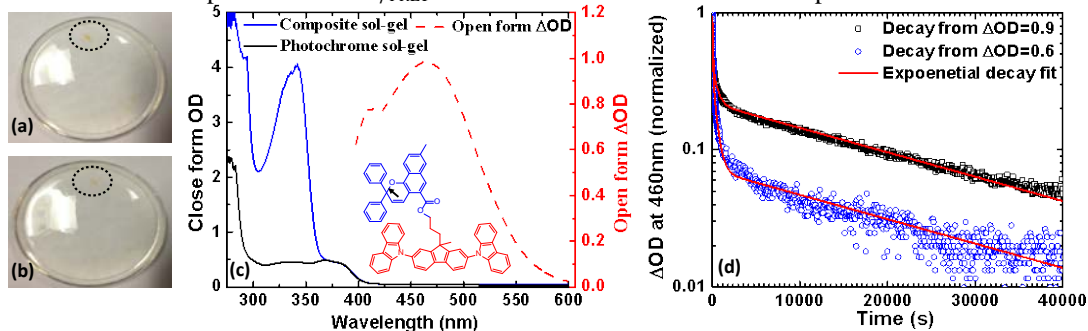


Fig. 1. (a) 2PA-FRET induced photochromism in a composite sol-gel. (b) Thermal reversing after ~ 4 minutes. (c) The closed-form linear absorption spectra of the composite sol-gel (blue solid) and pure photochromic sol-gel (black solid). The open-form ΔOD for composite sol-gel (red dash). The inset is the chemical structure of the composite molecule with donor moiety (bottom red) and acceptor moiety (top blue). (d) The thermally reversing photokinetic measurement of the open-form ΔOD (460nm) of the composite sol-gel, recovering from fully excited mode ($\Delta OD=0.9$) and partially excited mode ($\Delta OD=0.6$), fit by a triple exponential decay with the same time constants.

2. Results and Discussion

Fig. 1a shows a photograph of the composite molecule doped sol-gel glass slab with concentration N_0 (0.6×10^{-3} M/L) thickness L (1mm), where the colored area (circled) is due to 2PA-FRET induced photochromism (excited by femtosecond pulses at 620nm). The color fades in ~ 4 minutes as a result of a thermally reversible process (Fig. 1b).

The photochromic transformation behaves as a C-O bond breaking/reforming between the closed- and open- forms (arrow marked in inset of figure 1c). From the closed-form linear absorption spectrum shown in Fig. 1c, the weak absorption band (370-400nm) of the composite sol-gel originates from the photochromic acceptor moiety and the strong absorption (300-370nm) is contributed by the donor moiety. Upon excitation, the open-form molecule shows a broad absorption band (400-600nm) with peak absorbance (ΔOD) ~ 1 at 460nm. The thermally reversible process of the composite sol-gel was studied by tracking ΔOD spontaneously decaying after the excitation is blocked at room temperature. As shown in Fig. 1d (logarithm scale), the normalized ΔOD decays from the fully excited mode ($\Delta OD_{t=0} = 0.9$) and the partially excited mode ($\Delta OD_{t=0} = 0.6$), both fit using a triple exponential decay function with the same three time constants – 63s (τ_1), 530s (τ_2) and 24400s (τ_3). The results indicate that open-form isomers with different thermal stabilities are formed upon excitation.

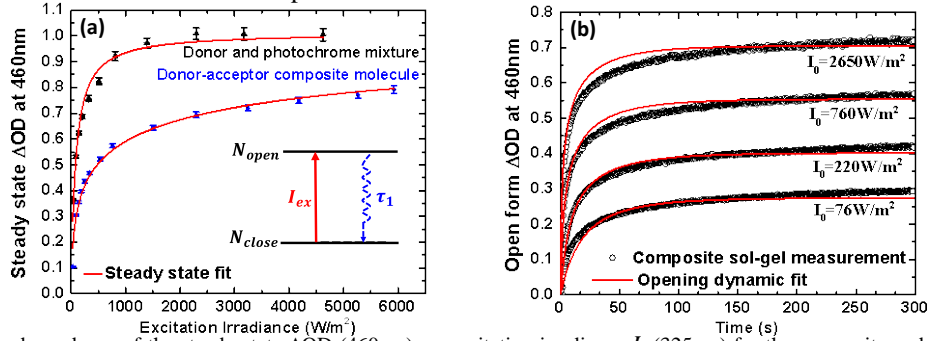


Fig. 2. (a) The dependence of the steady state ΔOD (460nm) on excitation irradiance I_0 (325nm) for the composite and the mixture doped sol-gel, fit by a 2-level model (inset) to obtain ϕ_{total} (from the composite sol-gel) and ϕ_{PC} (from the mixture sol-gel). (b) The opening photokinetic measurements for the composite sol-gel with different excitation irradiances are fit by the 2-level model.

To determine the FRET efficiency within the composite molecule, we developed a 2-level model in which the closed- and open- molecular forms are treated as ground and excited states (shown as the inset of Fig. 2a). Then the conventional rate equation approach is applied to describe closed- (N_{close}) and open- (N_{open}) form population changes as a function of input excitation irradiance (I_0), time (t) and sample penetration depth (z), as expressed in Eq. (1) by only taking into account the fastest thermal reversing time constant (τ_1) for the relaxation process:

$$\frac{dN_{open}(I_0, z, t)}{dt} = \alpha_c(I_0, z, t) \frac{I_{ex}(I_0, z)}{h\nu} - \frac{N_{open}(I_0, z, t)}{\tau_1} \quad (1)$$

Knowing the closed- and the open- forms have the same absorption cross section, σ_c , at the excitation wavelength 325nm from solution measurements [3], the excitation irradiance $I_{ex}(I_0, z)$ becomes time independent in the sol-gel. The effective closed-form absorption coefficient $\alpha_c(I_0, z, t)$ is defined as $(N_0 - N_{open}(I_0, z, t))\sigma_c\phi_{total}$. From Fig. 1c, the excitation photons (325nm) absorbed by the composite molecules are distributed 87% to donors and 13% to acceptors respectively, so ϕ_{total} can be expressed as $0.87\phi_{FRET}\phi_{PC} + 0.13\phi_{PC}$. By solving $N_{open}(I_0, z, t)$ from Eq.

(1), the ΔOD for the entire sample can be calculated from $\varepsilon \int_0^L N_{open}(I_0, z, t) dz$, where ε is the open-form molar absorptivity (460nm). Fig. 2a shows the open-form steady state measurement by varying I_0 , in which ΔOD increases with larger I_0 and reaches a maximum value due to ring-opening saturation. The 2-level model gives 5% ϕ_{total} from the fit for the composite sol-gel, and 15% ϕ_{PC} from the fit for the mixture sol-gel (donor and photochrome mixed without chemical bond), which results in 23% ϕ_{FRET} . Fig. 2b shows the accumulative opening time dynamics of the composite sol-gel excited from complete closed-form with different 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 discrepancy 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.

3. Conclusions

2PA-FRET induced photochromism has been demonstrated based on a sol-gel matrix doped with the donor-acceptor composite photochromic molecules. We observe open-form isomers with different thermal stabilities being formed upon excitation. By applying a 2-level model analysis, the FRET efficiency (23%) can be estimated from the simple UV-excitation (1PA) based photokinetic measurements.

4. References

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