Ultrafast excited-state dynamics associated with the photoisomerization of a cyanine dye

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The ultrafast excited-state dynamics of a cyanine dye, 3,3′-bis(3-sulfopropyl)-5,5′-dimethoxy-thiacyanine triethylaminium salt, was investigated by using conventional time-resolved fluorescence up-conversion technique. The fluorescence decay can be well described as tri-exponential kinetics, which indicates the excited-state population decays through the bond-twist, vibrational and radiative relaxation channels. Further analysis shows that the contributions of the three relaxation channels to the fluorescence decay demonstrate very different change with increasing the fluorescence wavelength, through which the detailed dynamics at different regions in the excited-state potential energy surface can be retrieved. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4759264]

I. INTRODUCTION

Light-induced trans-cis isomerization is one of the simplest chemical reactions, which is crucial in vision[1,2] and in the photoreception of plants and some bacteria.[3] It is also an important example for the research of the ultrafast excited-state dynamics,[4] which is a key for the possibility of using ultrafast laser pulse to control the chemical reaction. In the last several decades, as a model system, cyanine dyes have been extensively investigated for a detailed understanding of the excited-state dynamics during the photoisomerization process.[5–10] For these cyanine dyes, the dynamics of the photoisomerization reaction can be modeled as a continuous downhill motion of the nuclear wavepacket on a barrierless monotonously sloping potential energy surface (PES). However, the ultrafast excited-state dynamics in reality is much more complicated because the molecules have many vibration freedoms, which lead to a multi-dimensional excited-state dynamics. Therefore, for a long time, it was a challenging task to disentangle the ultrafast excited-state dynamics and present a clear picture of the wavepacket motion during the photoisomerization process.

In 1983, Bagchi, Fleming, and Oxtoby proposed a one-dimensional model called BFO theory for clarifying the excited-state dynamics of the photoexcited cyanine dyes.[11] As is depicted in Fig. 1(b), the ground state PES (S_0) features a high barrier separating the two isomers, while the excited state PES (S_1) is assumed to be a barrierless harmonic type. The trans isomer A in the equilibrium ground state is photo-excited into the Franck-Condon region to form a nuclear wavepacket in the S_1 surface. Then, the nuclear wavepacket undergoes a very fast bond-twisting nonradiative relaxation (k_{nr}) to the "sink" region, where an internal conversion (IC) process occurs intensely, subsequently followed by the ground state relaxation to the cis isomer B or back to the trans isomer A. Besides the bond-twist relaxation channel, the excited-state population also relaxes through another radiative channel (k_r), which produces emission. According to the BFO model, Sundström found the excited-state population shows a bi-exponential decay process,[5] of which the fast component was assigned to the bond-twist motion and the slow one to the IC process. BFO theory is a simplified model because it ignores the role of the molecular vibration relaxation. In 2005, theoretical calculations carried out by Hunt and Robb[4] demonstrated that photoisomerization of a cyanine dye is dynamically controlled by the extended trans-cis conical intersection (CI) seam, therefore the IC process takes place over a complete range of twist angles, but not at the "sink" point only. According to the Hunt and Robb's model (see the multi-dimensional scheme in Ref. 4), the vibrational motion along the non-reactive coordinate ("perpendicular" to the reactive twist-angle coordinate) plays an important role in the photoisomerization reaction for a cyanine dye, which suggests the excited-state dynamics should be analyzed in a multi-dimensional frame. Dietzek *et al.* confirmed the importance of the vibrational motion during the trans-cis reaction through an optimal control experiment,[12] but it is a nontrivial task to extract the detailed excited-state dynamics through that experimental scheme. Recently, by using a pump-dump-probe spectroscopy scheme, Wei *et al.*[13] successfully "visualized" the excited-state dynamics of a cyanine dye in specific time scale, which provides a strong proof for Hunt and Robb's theory.

However, some ambiguity was introduced in Wei's experiment[13] because the dump beam certainly disturbs the molecular system besides the function of dump, therefore, Wei *et al.* had to set different timing between the pump and dump pulses at different probe wavelength to assume the disturbance gone, in addition, Wei's experiment did not provide

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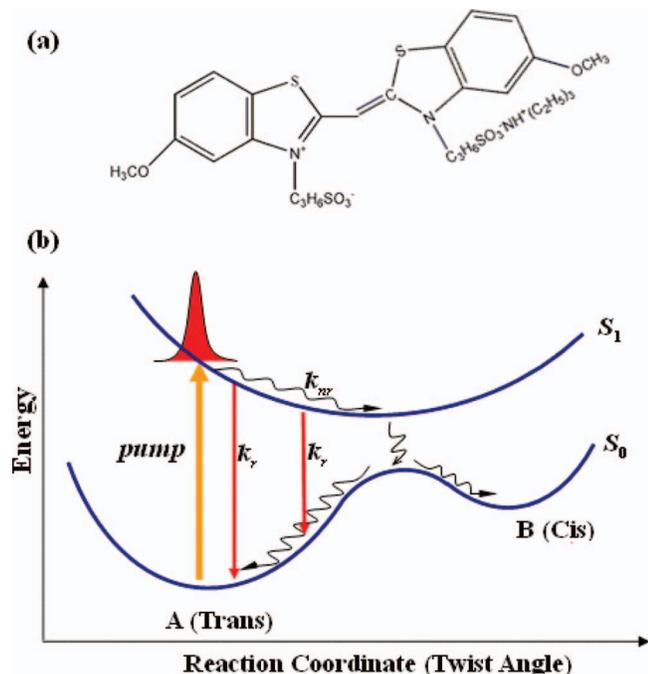
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FIG. 1. (a) The structure diagram of the working dye. (b) Schematic one-dimensional representation for the ultrafast decay during the trans-cis isomerization of the dye (for details, see the text).

much information on the vibrational relaxation along the S_1 surface for the photo-excited cyanine dye. For directly disentangling the detailed excited-state dynamics, in this report, we carried out a further investigation on the excited state dynamics of a cyanine dye, 3,3′-di(3-sulfopropyl)-5,5′-di(methoxy)-thiacyanine triethylaminium salt (structure diagram shown in Fig. 1(a)), by using conventional time-resolved fluorescence up-conversion technique. Different from the previous reports where the one-dimensional BFO model was employed,[5,6,14] we analyzed the excited-state dynamics of the dye in multi-dimensional frame. We found the fluorescence decays can be well described as tri-exponential kinetics. Our experimental result demonstrates that the ultrafast excited-state dynamics of the cyanine dye along the reactive and non-reactive coordinates can be directly discriminated by proper analysis of the transient fluorescence spectrum.

II. EXPERIMENTAL

The working dye, 3,3′-di(3-sulfopropyl)-5,5′-di(methoxy)-thiacyanine triethylaminium salt, was synthesized, purified, and characterized according to the method given in Refs. 6 and 15. The concentration of the dye in water solution is selected as 5×10^{-5} M. For the similar thiacyanine system, theoretical calculations[16] demonstrated there is only a very small barrier ($\sim$120 cm^{-1}) in the minimum-energy path, but for other possible reactive path no barrier exists. Experimental investigations in literature suggested barrierless photoisomerization model is a good assumption for the thiacyanine.[6,14,17]

The transient fluorescence dynamics of the samples was measured by the femtosecond time-resolved fluorescence up-

conversion technique. The light source was a Ti:Sapphire laser (Mira 900F, Coherent) working with a pulse train output with 76 MHz repetition rate. The pulse duration (FWHM) is 120 fs and the central wavelength of the pulses locates at 820 nm. The average single pulse energy is about 30 nJ. The fundamental pulses were frequency doubled to generate second harmonic (410 nm) pulses using a 0.3 mm thickness type 1 BBO crystal. The second harmonic beam with single pulse energy of about 1 nJ was used to excite the dye sample to generate fluorescence. The remaining fundamental pulses as a gate were used to generate up-conversion signal. The detailed description of the experimental setup can be found in Refs. 6 and 14.

III. RESULT AND DISCUSSION

In Fig. 2, the steady absorption and fluorescence spectra for the dye solution were illustrated. The absorption and fluorescence peaks locate, respectively, at 415 nm and 508 nm. The steady absorption and fluorescence spectra of thiacyanine dye in different solutions had been discussed in detail in Ref. 17. The result demonstrated that there are two isomers coexisting for the thiacyanine sample, which is also proved by the ^{1}H-NMR spectrum.[15] The absorption spectrum in Fig. 2 has a shoulder around 440 nm which is caused by the vibronic progression and the fluorescence spectrum can be well deconvoluted into two Gaussian bands, which generally can be considered as the feature of the coexistence of the trans and cis isomers.[17,18]

For measuring the transient fluorescence dynamics of the dye solution, the fluorescence wavelength of 475, 485, 495, 505, 545, and 565 nm were selected, which correspond to the radiative transitions ($S_1 \rightarrow S_0$) occurring at spots ranging from around Franck-Condon region to around "sink" point in the excited-state PES. At the wavelength longer than 565 nm, the up-converted fluorescence signal is noisy because of the bad SNR. Anyway, it is known that there is a long-wavelength-limitation for the conventional fluorescence up-conversion technique,[13] i.e., we cannot directly get the transient fluorescence signal corresponding to the "sink" region. However, through the fluorescence investigations at selected
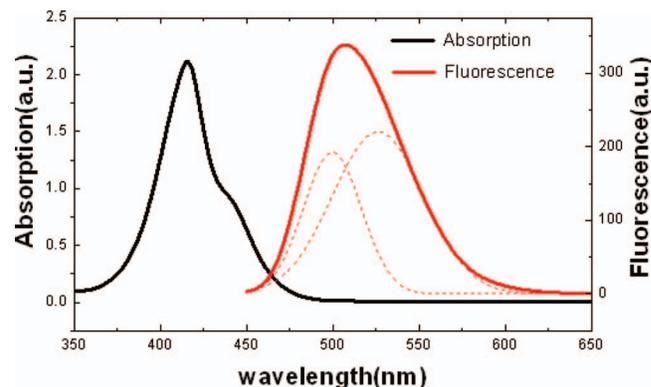

FIG. 2. Steady absorption and fluorescence spectra for the dye water solution with the concentration of 5×10^{-5} M. The fluorescence spectrum can be decomposed into two Gaussian bands, which are plotted in dotted-line.
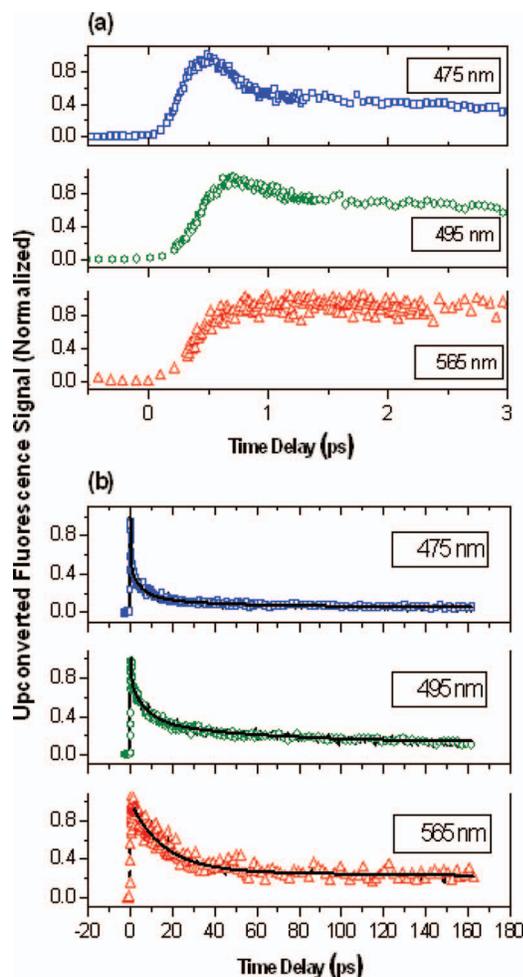
FIG. 3. Time-resolved up-converted fluorescence signals at the wavelength of 475 nm, 495 nm, and 565 nm. (a) The early time-delay region; (b) the complete time-delay scans, in which the solid lines are the fitted data by a multi-exponential decay function (see Table I).

TABLE I. Numerical result from fitting the fluorescence decays by using a tri-exponential decay function, $I(t) = I(0)(\alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) + \alpha_3 \exp(-t/\tau_3))$.

Wavelength (nm)	$\tau_1(ps)/\alpha_1$	$\tau_2(ps)/\alpha_2$	$\tau_3(ps)/\alpha_3$
475	0.28/0.57	5.31/0.31	36.03/0.12
485	0.31/0.53	6.23/0.31	48.67/0.16
495	0.42/0.29	7.84/0.45	60.22/0.26
505	0.51/0.20	8.61/0.60	76.17/0.20
545	−/0	14.75/0.76	109.17/0.24
565	−/0	15.64/0.90	117.08/0.10

decay function ($I(t) = I(0)(\alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) + \alpha_3 \exp(-t/\tau_3))$). In Fig. 3(b), the fitted curves at different fluorescence wavelengths were shown, and the numerical result was listed in Table I. It is to be mentioned that for the long wavelength fluorescence decay we fixed α_1 as zero to get a converged fitting, therefore it actually becomes a bi-exponential decay for the long wavelength fluorescence. For the fluorescence decays at short wavelength (475 nm–505 nm), according to the Hunt and Robb's theory[4] the ultrafast τ_1 component in sub-picosecond scale is assigned to the bond-twist decay along the reactive coordinate, the slower τ_2 component in picoseconds scale is assigned to the decay driven by the vibrational motion, and the longest τ_3 component in tens of picoseconds scale corresponds to the radiative relaxation. However, for the long wavelength (545 nm–565 nm) fluorescence, our numerical result shows that the τ_1 component corresponding to the bond-twist motion does not contribute to the population decay, which is because the long wavelength fluorescence corresponds to the transition occurring close to the "sink" region, where the bond-twist motion contributes to accumulate the excited-state population in the early time-delay and then the excited-state population decays mostly through the non-radiative IC process besides the minor radiative process—that is why the long wavelength fluorescence decay shows a bi-exponential kinetics. Through the above analysis, the excited-state dynamics of the cyanine dye was retrieved and the time scales of the excited-state dynamics agree well with Wei's experimental report.[13]

As list in Table I, the time constants of the τ_1, τ_2, and τ_3 increase monotonously with increasing the fluorescence wavelength, which is because the excited-state population closer to the Franck-Condon (high energy) region experiences a faster decay rate. In addition, with increasing the fluorescence wavelength, the weighting factors α_1, α_2, and α_3 of the three decay components demonstrate completely different change, which was illustrated in Fig. 4. For the bond-twist decay component, the weighting factor α_1 becomes monotonously smaller (from 0.57 to 0) with increasing the fluorescence wavelength (from 475 nm to 565 nm), which means the decay contribution from bond-twist motion shrinks more at the spot further away from the Franck-Condon region, consequently at the long wavelength limit, i.e., around the "sink" region the bond-twist decay contribution vanishes. That can be easily understood because the "downhill force" which drives the bond-twist motion along the reactive coordinate becomes smaller and smaller when the excited-state

wavelengths, we can conclude the excited-state dynamics corresponding to the "sink" region in the following discussions.

The time-resolved fluorescence dynamics varies obviously with different fluorescence wavelength, which was shown in Fig. 3(a). At the early time-delay region, the time-resolved fluorescence signals at 475 nm and 495 nm show a finite rise time of 490 fs and 700 fs, respectively, however, the fluorescence signal at 565 nm demonstrates an accumulation effect with a very slow rise time of about 1.5 ps, which is consistent with Sundström's observation.[5] According to the photoisomerization theories,[4,11] the initial photon-excited nuclear wavepacket at the Franck-Condon region undergoes a fast decay process (which was proved to be a wavepacket broadening and migrating process[13,19]) along the reactive coordinates, consequently, at the region further away from the Franck-Condon spot, the fluorescence signal produced by the transition of $S_1 \rightarrow S_0$ features a longer rise time.

After the rise time, the fluorescence signals at different wavelength demonstrate different decay behaviors (Fig. 3), which closely relate to the excited-state relaxation kinetics of the dye molecule. We found the time-resolved fluorescence decay can be fit very well by using a tri-exponential
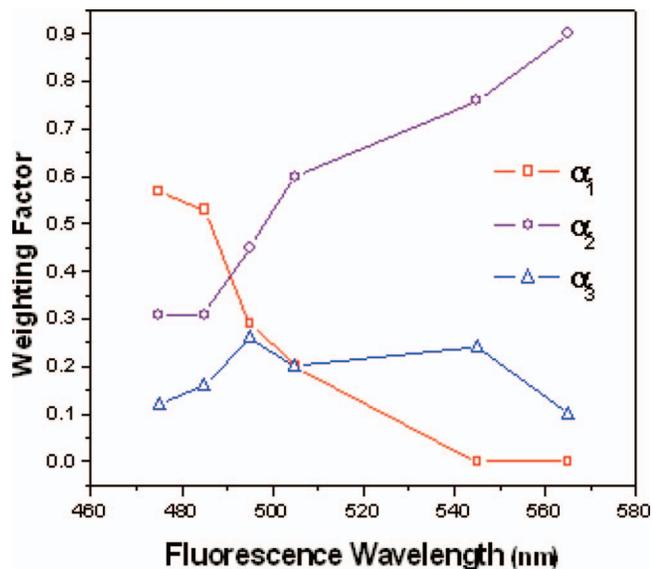
FIG. 4. The weighting factors α_1, α_2, and α_3 of the three decay channels at different fluorescence wavelength.

population migrates more and more distance away from the Franck-Condon region. On the contrary, the weighting factor α_2 becomes monotonously bigger with the fluorescence wavelength increasing, which means the decay contribution from the vibraional motion becomes more important when the excited-state population leaves the Franck-Condon spot further. From 475 nm to 565 nm, the α_2 factor grows from 0.31 to 0.9, therefore, it is reasonable to expect that at the long wavelength limit corresponding to the "sink" region, the α_2 factor will tend to be 1, which indicates there is no other decay process except for the intense non-radiative IC process at the "sink" region. For the weighting factor α_3, it shows a non-monotonous change with increasing the fluorescence wavelength. As depicted in Fig. 4, α_3 becomes bigger from 0.12 to 0.26 with the fluorescence wavelength ranging from 475 nm to 495 nm, and then with the wavelength further increasing, α_3 tends to shrink and at 565 nm it decreases to 0.1. That interesting behavior means that, in the high energy (around Franck-Condon) region, the excited-state population decays mostly through the non-radiative channels so that the radiative contribution is small as only ∼0.1; in the region further away (not very far away) from the Franck-Condon region, the non-radiative decay efficiency shrinks and the radiative efficiency grows to ∼0.26 (approximated maximum of the emission efficiency) at 495 nm, which is consistent with the steady fluorescence spectrum in Fig. 2, where the maximum of the fluorescence efficiency locates at around 500 nm; at last, in the low energy region close to the "sink" spot, the radiative efficiency drops greatly and it is reasonable to expect the radiative efficiency tends to be zero at the long wavelength limit where only the non-radiative IC decay exists.

It is to be mentioned that in the above analysis, the τ_2 component was assigned to the decay caused by the vibrational motion, which corresponds to the relaxation process along the coordinate "perpendicular" to the twist-angle axis. According to Hunt and Robb's theory,[4] the vibrational motion drives the excited-state population to relax to the CI seam (covering a complete range of twist angles) within picosecond time scale, where the non-radiative IC process occurs. In our numerical result, the τ_2 component exists for the fluorescence decays at all wavelength, i.e., the vibrational relaxation motion shows up at all twist angles, which agrees well with Hunt and Robb's theory.

IV. CONCLUSION

In this paper, it was demonstrated that with a tri-exponential decay model, the excited-state dynamics of a cyanine dye can be directly retrieved by using conventional time-resolved fluorescence up-conversion technique. The experimental result agrees well with Hunt and Robb's theory.[4] Moreover, through the analysis on the weighting factors of the three decay channels, the detailed excited-state dynamics of the cyanine dye at different energy region in the excited-state PES can be retrieved.

[1] R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, and C. V. Shank, Science **254**, 412 (1991).
[2] P. Kukura, D. McCamant, S. Yoon, D. B. Wandschneider, and R. A. Mathies, Science **310**, 1006 (2005).
[3] V. Sundström, Prog. Quantum Electron **24**, 187 (2000).
[4] P. A. Hunt and M. A. Robb, J. Am. Chem. Soc. **127**, 5720 (2005).
[5] A. Yartsev, J. Alvarez, U. Åberg, and V. Sundström, Chem. Phys. Lett. **243**, 281 (1995).
[6] W. Huang, S. Wang, H. Yang, Q. Gong, G. Xu, J. Xiang, C. Chen, and W. Yan, J. Chem. Phys. **117**, 6614 (2002).
[7] B. Dietzek, B. Bruggemann, T. Pascher, and A. Yartsev, Phys. Rev. Lett. **97**, 258301 (2006).
[8] C. S. M. Allan, B. Lasorne, G. A. Worth, and M. A. Robb, J. Phys. Chem. A **114**, 8713 (2010).
[9] B. Dietzek, T. Pascher, and A. Yartsev, J. Phys. Chem. B **111**, 6034 (2007).
[10] A. Weigel, M. Pfaffe, M. Sajadi, R. Mahrwald, R. Improta, V. Barone, D. Polli, G. Cerullo, N. P. Ernsting, and F. Santoro, Phys. Chem. Chem. Phys. **14**, 13350–13364 (2012).
[11] B. Bagchi, G. R. Fleming, and D. W. Oxtoby, J. Chem. Phys **78**, 7375 (1983).
[12] B. Dietzek, B. Bruggemann, T. Pascher, and A. Yartsev, J. Am. Chem. Soc. **129**, 13014 (2007).
[13] Z. Wei, T. Nakamura, S. Takeuchi, and T. Tahara, J. Am. Chem. Soc. **133**, 8205 (2011).
[14] T. Zhang, C. Chen, Q. Gong, W. Yan, S. Wang, H. Yang, H. Jian, and G. Xu, Chem. Phys. Lett. **298**, 236 (1998).
[15] Y. Tang, J. Feng, J. Xiang, C. Chen, W. Yan, and G. Xu, Chin. J. Magn. Reson. **18**, 161 (2001).
[16] R. Improta and F. Santoro, J. Chem. Theory Comput. **1**, 215 (2005).
[17] D. Noukakis, M. V. Auweraer, S. Toppet, and F. C. D. Schryver, J. Phys. Chem. **99**, 11860 (1995).
[18] M. R. V. Sahyun and J. T. Blair, J. Photochem. Photobiol., A **104**, 179 (1997).
[19] B. Dietzek, A. Yartsev, and A. N. Tarnovsky, J. Phys. Chem. B **111**, 4520 (2007).