ARTICLE

Ultrafast Energy Transfer in Artificial Antenna Molecule Measured by Transient Fluorescence Spectroscopy

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We have reported previously the ultrafast energy transfer process with a time constant of 0.8 ps from a monomeric to a dimeric subunit within a perylenetetracarboxylic diimide trimer, which was derived indirectly from a model fitting into the transient absorption experimental data. Here we present a direct ultrafast fluorescence quenching measurement by employing fs time-resolved transient fluorescence spectroscopy based on noncollinear optical parametric amplification technique. The rapid decay of the monomer's emission due to energy transfer was observed directly with a time constant of about 0.82 ps, in good agreement with the previous result.

Key words: Noncollinear optical parametric amplifier, Transient fluorescence, Perylenetetracarboxylic diimide trimer, Artificial antenna molecule, Energy transfer

I. INTRODUCTION

Recently, a novel transient fluorescence spectroscopic method based on noncollinear optical parametric amplifier (NOPA) has been developed for recording femtosecond time-resolved weak broadband fluorescence spectra [1−3]. With the benefit of high gain factor, high temporal resolution [4], low detection limit [5, 6], good spectral fidelity in a broad spectral range [7] and expand ability for near-IR fluorescence spectra measurement [3], it has a great potential in the study of ultrafast energy and electron transfer in chemical and biological process, as well as carrier relaxation dynamics in different kind of materials [8], and more practical applications are necessary to demonstrate its capability. In this work, we employ this method to directly measure the ultrafast fluorescence quenching in perylenetetracarboxylic diimide (PDI) trimer molecule in which an ultrafast energy transfer (ET) from the excited monomeric to the dimeric unit has been proposed before.

PDI trimer molecule has been synthesized for mimicking the ultrafast ET from a bacteriochlorophyll (BChl) monomer (B800) to BChl dimmer (B850) in a peripheral light-harvesting antenna complex (LH2) from the photosynthetic bacteria [9]. The trimer is linked by a triazine ring with a conformation such that two of the three PDI subunits in the trimer present a face-to-face stacked configuration while the third one appended acts as a monomer. The molecular structure of the PDI trimer and corresponding ET from the PDI monomeric to the dimeric subunit determined by the transient absorption measurement have been reported in our earlier work [10]. In analysis of the acquired transient absorption spectra, we employed the method of singular value decomposition (SVD) combined with global fitting procedure to resolve the absorption spectra of the related species and the corresponding kinetics based on a proposed monomeric/dimeric co-excitation model. This model involves a single photon excitation of both the monomeric and dimeric subunits with different probability, followed by different energy relaxation paths, and the derived ET time constant from the monomeric to the dimeric subunit is 0.8 ps, similar to that in LH2 (0.8−0.9 ps) [11]. However, due to the complexity of the data from transient absorption measurement, the process of the ET can not be revealed intuitively. Although the SVD method had been used, the final results such as the accuracy of ET rate constant strongly depended on the validity of the proposed model. Therefore a direct measurement of the ultrafast quenching of the fluorescence from the monomeric block within the trimer is necessary, which would give straightforwardly the time constant for the above ET process, and also provide evidence to support the proposed model in the previous work [10].

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II. EXPERIMENTS

The details of the synthesis and structure characterization have been reported in the previous work [10]. Femtosecond transient fluorescence measurements were conducted on a NOPA based time-resolved transient fluorescence spectrometer. The detail of its experimental setup has been reported elsewhere [3, 5]. Briefly, a 1 kHz Ti:sapphire regenerative amplifier (Hurricane, Spectra Physics) delivering 750 μJ energy per pulse with a pulse duration of 150 fs at 800 nm was employed as the primary beam source. The output beam was split into two parts. The one with energy about 300 μJ was frequency doubled, or alternatively used to pump a home-built NOPA to generate the excitation pulse for fluorescence with tunable wavelength. The fluorescence was collected by lens and then focused onto a 2-mm-thick BBO crystal, cut at θ_c=32°, φ_c=0° for the 400 nm pumped type I phase-matched NOPA. The other beam was frequency doubled as the pump beam for the BBO-NOPA. The seeded fluorescence photons would be amplified by the pump beam in the crystal. Then the amplified signal was collected by an objective lens coupled to an optical fiber, and recorded by a charge-coupled device (CCD) spectrometer (Acton).

All the compounds were dissolved in toluene at a concentration of 0.1 mmol/L for fluorescence measurements.

III. RESULTS AND DISCUSSION

The absorption and fluorescence spectra of the monomer, dimer and trimer dissolved in toluene have been reported in the previous work [10]. The relatively high intensity around the shorter wavelength absorption band of the dimer indicates the formation of the face-to-face stacked H-aggregates [12]. In addition, the fluorescence spectrum of dimer shows a broad tail extending to 750 nm in addition to a monomer's emission at 570 nm, which can be assigned to the excimer-like emission which is characterized by red-shifted emission band, low fluorescence quantum yield, and longer fluorescence lifetime [13−15]. For the trimer, only a broad emission band in the range of 550−750 nm with a fluorescence lifetime of 22 ns was detected, which can be attributed to the excimer-like emission rather than that of monomer [16, 17]. In other words, the fluorescence of monomer has been quenched effectively, indicating the existence of the ET from monomeric subunit to dimeric subunit within the trimer.

The time-resolved fluorescence of trimer as well as monomer were measured. For both the monomer and the trimer, the samples were excited at 400 and 532 nm respectively. We found that the fluorescence decay kinetics curves are almost the same regardless of the different excitation wavelength. The fact indicates that the energy relaxation from higher excited state to the lower excited state of monomer is so fast that the relaxation time is beyond the temporal resolution of the instrument, confirming our previous model [10].

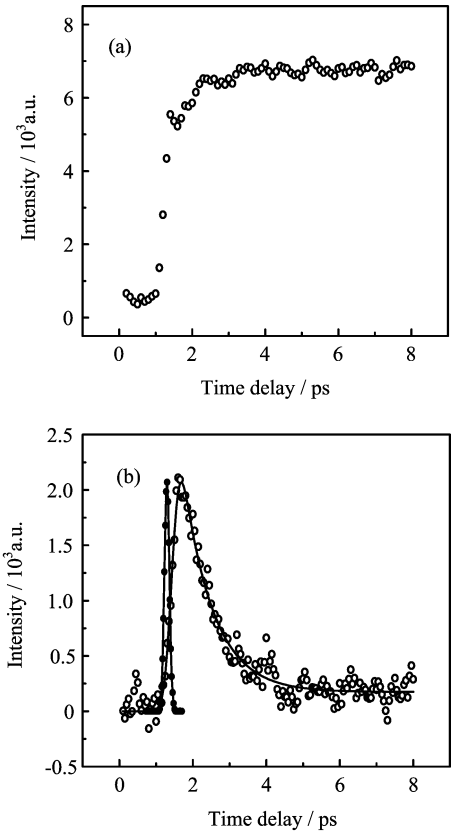

FIG. 1 (a) Fluorescence kinetics of monomer excited at 532 nm and probed at 575 nm. (b) Fluorescence kinetics (open circle) and IRF (solid circle) of trimer excited at 400 nm and probed at 575 nm. Solid line: the fitting curve. The fitting result reveals a lifetime constant of 0.82 ps.

The acquired fluorescence decay kinetics of monomer and trimer are shown in Fig.1. The monomer is excited at 532 nm and probed at 575 nm which is close to the emission maximum of the monomer (Fig.1(a)). The lifetime of monomer is about 4 ns, it is expected that there should be no obvious intensity change of the fluorescence within the probe window of 8 ps (also in a detection window of 100 ps) as shown in Fig.1(a). In contrast, the fluorescence decay kinetics of the trimer presents an ultrafast decay feature shown in Fig.1(b). Considering the convolution of the instrument response function (IRF) which is the convolution of the shape of the exciting pulse and the detector response, we obtained a decay time constant of 0.82 ps by fitting of the fluorescence kinetics with a mono-exponential decay function.

Furthermore, the transient fluorescence spectra of the monomer as well as trimer at 0.1 ps after excitation were recorded as shown in Fig.2. The resemblance between the two transient emission spectra strongly suggests

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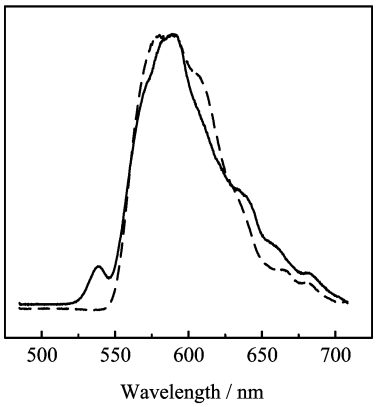

FIG. 2 Comparison of the transient fluorescence spectra between the monomer (dashed line) and trimer (solid line).

that the fluorescence of the trimer at the early time after excitation is mainly contributed by the monomer. This can be understood that owing to the lower quantum yield (8%) and much longer life time (20 ns, which means less photons per unit time) of the dimer's emission, the detected transient fluorescence spectrum is mainly from the monomeric subunit within the trimer. Thus, the fluorescence decay kinetics as well as the transient fluorescence spectrum indicate that emission of the monomeric unit is quenched immediately after excitation due to ET from the monomeric to the dimeric subunit, giving a direct evidence supporting the result of our earlier transient spectroscopic study.

IV. CONCLUSION

With the help of the novel time-resolved transient fluorescence spectroscopic method, the ultrafast fluorescence quenching for the monomeric unit within the PDI trimer was observed directly, demonstrating the existence of energy transfer from a monomeric PDI to a covalently linked PDI dimeric subunit with a time constant of about 0.82 ps, in good agreement with the result from our previous transient absorption spectroscopic study. The current work also provides an example demonstrating the feasibility of the NOPA based time-resolved transient fluorescence spectroscopic method as a promising tool in the study of ultrafast time-resolved photochemical and photophysical emission processes.

V. ACKNOWLEDGMENTS

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