Supplementary Information

Excited-state dynamics of Si-rhodamine and its aggregates: Versatile fluorophore for NIR absorption

Sooyeon Kim, Mamoru Fujitsuka, Mikiji Miyata, Tetsuro Majima*

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047 (Japan)

Methods and Materials

Materials. Chemical reagents and solvents were purchased from Sigma-Aldrich Chemical Co., Tokyo Chemical Industries, Nacalai Tesque, and Wako Pure Chemical, and used without further purification. 2-Methylbenzene-replaced SiR (**Si-Me**) was synthesized according to the method of Koide *et al.*,² while **TMR-An**, **SiR-An**, and **Si-DMA** were synthesized as described in our previous paper (all chemical structures are depicted in Figure 1 in the main text).^{11, 13} Dyes stored in dimethyl sulfoxide at -20 °C in the dark were used in all spectroscopic experiments.

Steady-state measurements. Methanol (spectroscopic grade), phosphate-buffered saline (PBS) at pH 7.5 without Ca²⁺ and Mg²⁺ (both purchased from Nacalai Tesque), or MilliQ water were used as the solvent. Ground-state absorption and fluorescence emission spectra were measured using Shimadzu UV-3100 and Horiba FluoroMax-4 spectrometers, respectively.

Measurement of fs-LFP. Transient absorption spectra of Si-Me, SiR-An, Si-DMA, and TMR-An dissolved in methanol or MilliQ water on the sub-ps to ns time scale were measured by the pump-and-probe method using a regenerative amplified titanium sapphire laser (Spectra Physics, Spitfire Pro F, 1 kHz) pumped by a Nd:YLF laser (Spectra Physics, Empower 15). In methanol, where fluorophores are present as a monomer, solutions of Si-Me, SiR-An, Si-DMA, TMR-An were prepared with a concentration so that their absorbance was 1.2, 1.2, 0.9, and 1.2 with a 0.2cm path length at 650 nm, respectively ([Si-Me], [SiR-An], and [Si-DMA] were ~65 µM, while [TMR-An] was 100 µM). SiR-An H-aggregate sample was prepared in MilliQ water at such a concentration that their absorbance was approximately 0.37 at 650 nm, while that of J-aggregate sample was prepared in MilliO water with [NaCl] = 20 mM and their absorbance was approximately 1.05 at 740 nm with a 0.05-cm path length; that is, $[SiR-An] = 100 \mu M$ both for Hand J-aggregate samples. An excitation pulse at 650 or 740 nm (the former was used for monomer and H-aggregate samples, and the latter for J-aggregate samples) was generated by an optical parametric amplifier (Spectra Physics, OPA-800CF). A white continuum pulse, which was generated by focusing the residual of the fundamental light onto a rotating CaF₂ plate after a computer-controlled optical delay, was divided into two parts and used as the probe and reference lights, the latter of which was used to compensate for the laser fluctuation. Both probe and reference lights were directed through a sample cell with a path length of 0.1 cm and then detected with a charge-coupled device detector equipped with a polychromator (Solar, MS3504). To determine the transient extinction coefficient as shown in Table 1 in the main text, we prepared three samples with the same concentration and measured on the same day,

Measurement of ns-LFP. The nanosecond transient absorption measurements were performed using the laser flash photolysis technique. Briefly, the third-harmonic oscillation (355 nm, fwhm of 4 ns) from a Q-switched Nd:YAG laser (Continuum, Surelite II-10) was used for the excitation light. The light from a xenon flash lamp (Osram, XBO-450) was focused into the sample solution for the transient absorption measurement. Time profiles of the transient absorption in the UV–vis region were measured with a monochromator (Nikon, G250) equipped with a photomultiplier (Hamamatsu Photonics, R928) and digital oscilloscope (Tektronics, DPO 3054). Each decay profile was collected by averaging 64 times.

Pulse radiolysis of Si-Me. Pulse radiolysis experiments were performed using an electron pulse (28 MeV, 8 ns, 0.7 kGy per pulse) from a linear accelerator at Osaka University. In the present study, a solution of Si-Me (200 µM) in pH 7.4 PBS containing tert-butanol (100 mM) to generate the SiR radical anion (SiR^{•-}) was prepared, and then the SiR radical cation (SiR^{•+}) was prepared by adding Na₂S₂O₈ (3 mM).¹ Transient absorption measurements during pulse radiolysis were carried out using a nanosecond photoreaction analyzer system (Unisoku, TSP-1000). A pulsed 450-W Xe arc lamp (Ushio, UXL-451-0) was used as a monitor light source. The monitor light that passed through the sample solution was focused on the entrance slit of a monochromator (Unisoku, MD200) and detected with a photomultiplier tube (Hamamatsu Photonics, R2949) and transient digitizer (Tektronix, TDS580D). Transient absorption spectra were measured using a photodiode array (Hamamatsu Photonics, S3904-1024F) with a gated image intensifier (Hamamatsu Photonics, C2925-01) as a detector. Transient extinction coefficients (ε) of SiR⁺⁺ and SiR⁻⁻ were calculated by comparison with the concentration of the initially appeared transient species of persulfate (SO₄⁻) and hydrated electrons (e_{aq}^{-}), respectively (ε of SO₄⁻⁻ and e_{aq}^{-} are $1,600 \text{ M}^{-1} \text{ cm}^{-1}$ at 450 nm² and 23,000 M⁻¹ cm⁻¹ at 700 nm,³ respectively). Both SiR⁺⁺ and SiR⁺⁻ spectra were measured 5 μ s after a pulse.

Supporting Tables and Figures

Material	$\Phi_{ m fl}$	$ au_{ m fl}$ / ns	$k_{\rm rad}$ / s ⁻¹	$k_{\rm nr} / { m s}^{-1}$
Si-Me	0.32	3.56	$0.9 imes 10^8$	1.9 × 10 ⁸
SiR-An	0.05	0.75	$0.9 imes 10^{8}$ a	$1.8 imes 10^{9 \text{ b}}$

Table S1. Decay rates of Si-Me and SiR-An calculated from Φ_{fl} and τ_{fl} in methanol.

^aBecause the fluorophores of Si-Me and SiR-An are the same, k_{rad} of Si-Me and SiR-An were assumed to be the same when calculating k_{nr} ; ^bThis value was calculated based on τ_{fl} of SiR-An.



Figure S1. Schematic diagram of two interacting transient dipole moments and energy splitting, and the formation of an H- or J-aggregate depending on the angle (θ) between the longitudinal axis of the monomer transition moments. Based on exciton theory, two interacting molecules in a plane exhibit electron overlap, leading to energy level splitting. When the angle (θ) between the longitudinal axis of the monomer transition moments is 54.7° < θ < 90°, electronic transition to the higher energy level is permitted, resulting in a blue shift of absorption maxima and non-fluorescent H-aggregate. Meanwhile, if θ is 0° < θ < 54.7°, electronic transition to the lower energy level is permitted, resulting in a blue shift of absorption and fluorescence spectrum.



Figure S2. Absorption spectra of (a) $10 \,\mu\text{M}$ **TMR-An** and (b) $10 \,\mu\text{M}$ **SiR-An** in methanol (pathlength: 2 mm).



Figure S3. Changes in (a) absorption and (b) fluorescence spectra of **SiR-An** in MilliQ water upon addition of 0, 50, and 100 mM NaCl (black, red, and blue, respectively). [**SiR-An**] = 5 μ M, path length: 0.2 cm, and λ_{ex} = 640 nm. Spectra were measured around 30 min after sample preparation. As shown in Figure S3a clearly, the addition of halide ion induces the formation of J-aggregate of SiR as well as anthracene moieties (black arrows). Without halide ion (black line), **SiR-An** forms H-aggregate, which is characterized by the appearance of blue shoulder band at around 615 nm. The molecular extinction coefficients (ε) shown in Figure S3a are simply calculated by absorbance divided by the concentration of monomer and path length. Thus, it is notable that this molecular

extinction coefficient is reasonable only when the same concentration of **SiR-An** and incubation time are used for the preparation. We obtained the ε of TMR-An aggregates through the same method (Figure S5a). A red asterisk in Figure S3b indicates J-aggregate emission of **SiR-An**.⁴ (c) (Left) Extended view of the X-ray crystal structure of **SiR-An** aggregate. (Right) Geometry of two neighboring **SiR-An** molecules depicted in a black square.⁴ Those data have been reported in our previous paper,⁴ and presented here with slight modifications to help understanding of readers.



Figure S4. (a) Transient absorption spectra of **Si-Me** in methanol from 0.4 to 71 ps (blue to red) after a laser pulse at 650 nm during fs-LFP. (b) Time profile of transient absorption decay at 430 nm (open circles) and biexponential fitting results (red lines) of **Si-Me** in methanol.



Figure S5. Calculated energy levels of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) and their distributions in **SiR-An** using the DFT calculation (B3LYP/6-31G(d,p) level).



Figure S6. (a) Changes in absorption and spectra of **TMR-An** in MilliQ water upon addition of 0, 50, and 100 mM NaCl (black, red, and blue, respectively). [**TMR-An**] = 5 μ M and path length: 0.2 cm. Spectra were measured around 30 min after sample preparation. Like **SiR-An**, **TMR-An** forms J-aggregate in the presence of halide ion as indicated by a red-shift and sudden increase in the extinction coefficient.⁴ As stated in the caption of Figure S3, we calculated the ε based on Beer-Lambert rule, and this data have been previously presented in the recent communication.⁴ (b, c)

Transient absorption spectra monitored at 0.4, 5.2, 17, 53, and 73 ps (black to red) after a laser pulse during the fs-LFP of the **TMR-An** monomer in methanol excited at 550 nm (15 μ J pulse⁻¹).



Figure S7. (a) Time profiles of transient absorption decay (open circles) and multiexponential global fitting results (green lines) of **SiR-An** H-aggregate determined from the transient absorption data shown in Figure 4a in the main text. A biexponential function ($\tau = 0.6$ and 16.8 ps) was used to fit the data. It should be noted that there was a long-lived component (around a few hundred ps) that remained after the fitting of H-aggregate data. (b) Transient absorption spectra of **SiR-An** H-aggregate from 0.4 to 71 ps (black to green) after a laser pulse at 650 nm during fs-LFP. Through global analysis of the spectra, three deconvoluted transient absorption spectra were obtained: the fast (16.8 ps), slow (a few hundreds), and negative species assigned to the SiR H-aggregate in the initially excite state, relaxed intermediate, and ground state bleaching, respectively.



Figure S8. Transient absorption spectra monitored at 0.4, 0.6, 0.8, 2.0, 5.0, 10, (insets) 20, 50, 100, 200, and 500 ps (black to red) after a laser pulse during the fs-LFP of the **SiR-An** J-aggregates in the aqueous solution excited at 740 nm, near to the maximum of the J-band, at approximately (a) 2.0 μ J pulse⁻¹ and (b) 290 nJ pulse⁻¹.



Figure S9. Transient absorption spectra monitored at 0.4 ps after a laser pulse during the fs-LFP of the **SiR-An** J-aggregates with different excitation intensities. For 15 and 2 μ J pulse⁻¹, the blue-shifted absorption band is more evident as compared to that of 0.04 μ J pulse⁻¹.



Figure S10. Time profile of positive transient absorption of **SiR-An** J-aggregates at 730 nm in the aqueous solution excited at 740 nm at 40 nJ pulse⁻¹. Red and blue lines are the fitting results based on one- (1D) and three-dimensional (3D) exciton-exciton annihilation (EEA) behavior, respectively.⁵⁻⁷ Although fitting results seem to be in accordance with the experimental data particularly during the initial 10 ps, the obtained diffusion constants of the exciton were not reasonable value, the maximum values of fitting results did not reach up to 1, and the deviation became larger at longer than 100 ps. The data were well matched with the three-exponential model (Figure 5b in the main text), which phenomenon has been reported in the previous studies.^{8, 9}

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