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The fluorescence behavior from SAM of dendron with rhodamine B as a center

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Abstract

We studied energy transfer between rhodamine B molecules centered in each corn-shaped dendrons that forms self-assembled monolayer (SAM) film on an Au substrate. A SAM film using dendron moiety as a spacer can change the distance between rhodamines depending on the size, so that the energy transfer from an initially photo-excited rhodamine to its surrounding molecules can be controlled. The absorption spectrum of a SAM film for each generation of dendron was measured to ascertain a linear correlation between the generation and the distance. Picosecond time-resolved fluorescence spectra showed clear differences in the fluorescence decay dynamics between third-generation (G3) and fourth-generation (G4) dendron SAM films. In addition, we found that "dry" or "wet" dendron SAM considerably influenced fluorescence behavior. As a result, the use of "wet" G4 SAM is suitable in preserving photo-excitation energy. This is because it gave almost equal dynamics to G4 dendron in the dilute solution and prevented deactivation by energy dissipation.

Keywords: Energy transfer; Dendron; Self-assembled monolayer; Time-resolved fluorescence spectrum

1. Introduction

Photochemical reactions controlled at one molecular level could open a unique way to fabricate nano-scale molecular devices. When the energy transfer from a photo-excited molecule on a position-sensitive nano-probe to a particular acceptor within a self-assembled monolayer (SAM) film on a substrate is caused, and the excited acceptor undergoes a unimolecular reaction, we can obtain a product on a designed position in the SAM. By repeating this process with selecting the SAM position, a series of products organized in an order is formed. Our preliminary results have already demonstrated that triplet–triplet energy transfer occurred using SAM films on substrate [1]. In electric current induced chemical reactions, a similar procedure has been investigated using STM probes [2]. However, they are restricted because they need conductive surfaces. In this scheme, we can use the insulator surface.

Although various experimental conditions should be examined to accomplish the above scheme, as a first step, we studied the energy transfer between rhodamine B molecules centered in each corn-shaped dendron that forms a SAM film on an Au substrate. This model explores whether a photo-excited molecule keeps the excitation energy without dissipating it to surrounding molecules. We tried to control singlet–singlet energy transfer because resonant energy transfer can easily occur among the same kind of molecules in a SAM. The Förster mechanism explains the rate of energy transfer between singlet molecules is inversely proportional to the sixth power of distance [3]. To prevent energy transfer from a photo-excited molecule to its surrounding molecules, dye molecules in the dendron SAM must be positioned quite far from each other. It is known that a SAM film provides regular and low-dimensional ordered structures [4–6]. The use of a corn-shaped dendron as a spacer is expected to control the distance between dye molecules by varying the size of dendron moiety.

In general, the fluorescence lifetime directly reflects the rate of relaxation processes. When energy transfer occurs between rhodamines in a small dendron SAM, the fluorescence lifetime could be shorter than that in isolated case. On the contrary, the larger spaced distance would prevent the energy transfer and result in a longer lifetime. The measurement of time-resolved fluorescence will help determine the situation around a photo-excited rhodamine in a dendron SAM film.

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2. Experimental details

Each generation from first-generation (G1) to fourth-generation (G4) dendron with a rhodamine B molecule as the center was synthesized using the procedures described elsewhere [7]. The synthesized product had a methylthio group at the peripheral sites as multiple anchors to the surface of substrate. The molecular structure is shown in Fig. 1.

We formed dendron SAM films by soaking an Au-sputtered film substrate in a 1 μM dichloromethane solution of dendrons for 72 h, followed by gentle rinsing with a solvent. To examine the site isolation controllability of the dendron SAM films, absorption spectra obtained by comparing the reflectance between coated and uncoated parts of the Au substrate using a visible spectrophotometer (Hitachi, U-4000 with a 5° speculum reflectance attachment) were analyzed. The stationary fluorescence spectra upon 530 nm excitation were measured using a fluorescence spectrometer (Hitachi, F-4500).

Time-resolved fluorescence spectra were also measured by combining a microscope (OLYMPUS, IX70) and a polychromator (Acton, SP150) with a time-gated image-intensified charge-coupled device (ICCD) camera (LA VISON, Picostar). The pump pulse used was the second harmonic (530 nm, 1 μJ/pulse) of optical parametric amplifier (OPA) signal wave with a regeneratively amplified femtosecond Ti:Sapphire laser (Spectra-Physics, Hurricane). The resolution was ca. 130 ps, which was determined by the gate width of the ICCD camera.

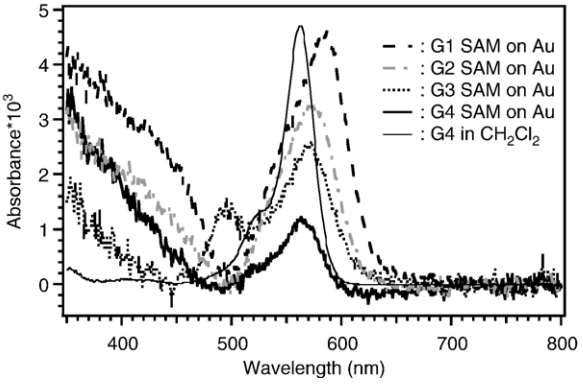

Fig. 2. Absorption spectra of G1 to G4 dendron SAM films obtained by comparing the reflectance between coated and uncoated parts of Au substrate. Absorption spectrum of G4 dendron in CH_2Cl_2 solution is also included.

3. Results and discussion

The absorption spectra of G1 to G4 dendron SAM films are shown in Fig. 2. The peak intensity of absorbance around 580 nm, which corresponds to the absorption band of rhodamine B, was found to be inversely proportional to the dendron

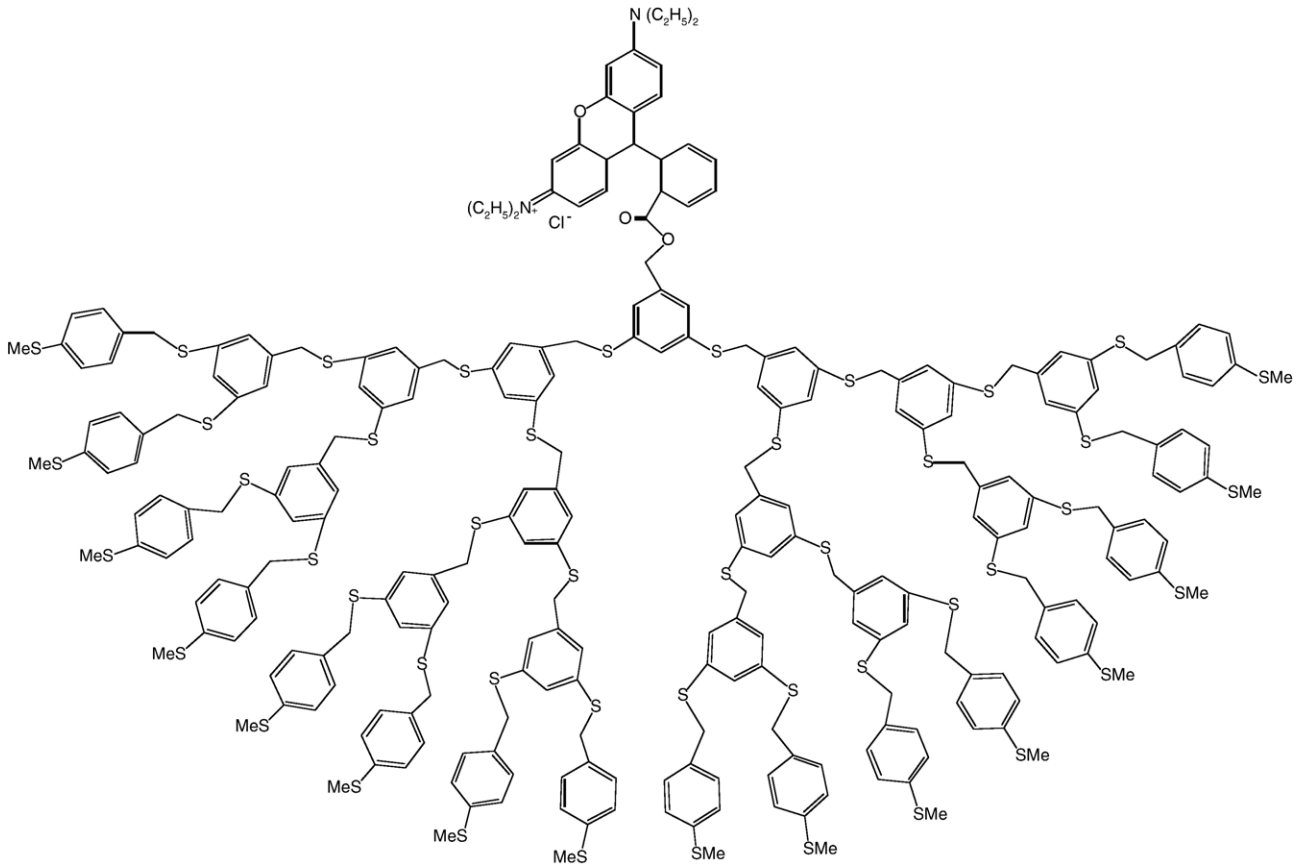

Fig. 1. Schematic structure of G4 dendron with a rhodamine B molecule as the center.