

Site-separation control using dendron molecular probes towards high-resolution photochemical reaction

Akira Otomo*, Hideki Miki, Isao Aoki, Shinro Mashiko

Kansai Advanced Research Center, National Institute of Information and Communications Technology, 588-2 Iwaoka, Nishi-ku, Kobe 651-2492, Japan

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Abstract

We propose molecular-scale photochemical-reaction control using triplet–triplet (T–T) energy transfer from a donor molecule attached on a probe to an acceptor on an insulator surface. We used a cone-shaped dendron molecule to avoid sensitizer self-quenching caused by the triplet energy migration within the probe surface. We demonstrated effective control of distance between functional sites on a surface using cone-shaped dendrons. The generation-three dendrons provide enough distance between the functional sites on the probe to reduce singlet energy transfer and it should control triplet energy migration. We also studied the feasibility of photochemical reactions on a substrate surface using a triplet sensitizer probe. We observed an efficient T–T energy transfer from Michler's ketone on the substrate to an acceptor molecule, cinnamoyl group, on the other substrate facing it. Approximately a quarter of the cinnamoyl groups were dimerized by triplet sensitization.

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1. Introduction

Nanoscale chemical-reaction control is expected to play an important role in building complicated molecular device structures and nanoscale lithography for semiconductor devices. Molecular self-assembly provides regular, low-dimensional ordered structures [1–3]. However, additional manipulation techniques, such as the scanning-probe-microscope (SPM) probe-assisted approach, are necessary to make realistic molecular devices, which should consist of various functional units in a controlled order. Electric-current induced chemical reactions have been investigated using STM probes [4]; however, they are limited to uses only on conductive surfaces. For non-conductive surfaces, a photochemical approach using a near field scanning optical microscope (NSOM) can be employed [5]. However, the resolution of NSOM is not fine enough for applications to single-molecular-scale reaction control. A

catalyst-coated probe is a promising device for realizing molecular-scale reaction control [6,7]. However, undesirable catalytic actions can occur, even during the surface observation period, and the reactions cannot be actively controlled.

Here, we propose a molecular-scale photochemical-reaction control using triplet–triplet (T–T) energy transfer from a donor molecule attached on a probe to an acceptor on the insulator surface. The key advantage of this scheme over other techniques is the temporal and spatial controllability that arises from the photo-assisted process and indirect excitation. Since the reaction occurs only during photo irradiation, surface characterization and reaction can be performed individually. Also the acceptor (i.e. the reactant) is never photo-excited directly, because the first excited singlet level for the acceptor can be higher than that of the donor. Furthermore, since T–T energy transfer (which was first described by D.L. Dexter [8]) occurs only within the range of a few nanometers, the reaction is highly localized in the vicinity of the donor molecule attached to the SPM probe (Fig. 1a). However, a low surface density of the donor molecules on the probe is

* Corresponding author. Tel.: +81 78 969 2255; fax: +81 78 969 2259.

E-mail address: akira_o@nict.go.jp (A. Otomo).

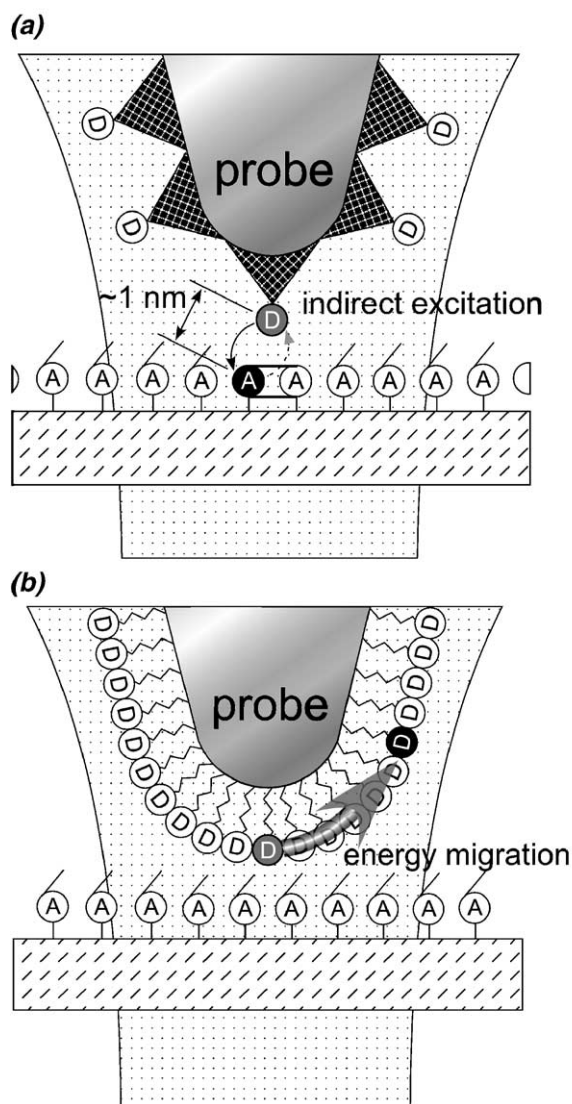


Fig. 1. Schematic representation of (a) T–T energy transfer from a dendron attached to a probe, and (b) energy migration between densely packed donor molecules on a probe.

essential to carry out molecular-scale reaction control in this scheme. An efficient T–T energy transfer to an acceptor molecule cannot be obtained from densely packed donors because the triplet energy migration between the donor molecules is dominant in this case (Fig. 1b). Also, the spatial resolution is never smaller than the size of the probe tip. A low surface density of the donor molecules is essential to avoid quenching due to energy migration and to improve the spatial resolution, which can be finer than the size of the probe tip.

Dendrimers are a new class of polymers whose three-dimensional structures are highly controllable. The site isolation effect of spherical-shaped dendrimers has been studied extensively [9], and we have demonstrated an improvement in the optical properties of the molecules in severe environments [10–13]. However, the focal point of the dendrimer is fully covered by peripheral molecules.

Therefore, site isolation and efficient energy transfers cannot be achieved simultaneously using spherical dendrimers. We attempted to use a cone-shaped dendron as an anchor to control the spacing between donor molecules on the probe surface. The dendron's cone shape is expected to act as a spacer isolating the functional site at the focal point from both the surface and the neighboring functional molecules. We studied feasibility of the reaction using a T–T energy transfer between a donor and an acceptor, individually attached to facing substrates. We also studied the controllability of the spacing of the functional site on the surface using a dendron anchor.

2. Experimental details

We synthesized dendrons (Fig. 2a) that had a methylthio group at the peripheral sites as multiple anchors to the surface. They had a rhodamine B (RhB) molecule at the focal point as a fluorescent probe. The dendron's cone shape is expected to act as a spacer isolating the functional site at the dendron's focal point from both the surface and the neighboring functional molecules. The self-assembled monolayer (SAM) film was made by immersing an Au-sputtered film substrate in 10 μM toluene solutions of the dendrons for 10 h, followed by a gentle rinsing with toluene. We examined the site-isolation controllability of the cone-shaped dendrons by measuring the absorption and fluorescent properties of the SAM films from several generations of dendrons on Au-sputtered film substrates. We evaluated the absorption spectra of the SAM films by comparing the reflectance spectra taken by an ultraviolet/visible (UV/VIS) spectrophotometer (Hitachi, U-4000 with a 5° specular reflectance attachment) between the coated and uncoated part of the Au substrate. The fluorescent spectra were taken by excitation at 530 nm using a fluorescence spectrophotometer (Hitachi, F-4500).

A cinnamate dendrimer (Fig. 2b) was synthesized as the acceptor molecule, and its monolayer film was fabricated using the Langmuir–Blodgett (LB) technique. A 0.1 mM chloroform solution was spread on the water surface, and the film was compressed at a pressure of up to 18.0 mN/m. Then, the film was transferred to a fused silica substrate (Sub-A) that was polished to $\lambda/20$. As the donor molecule we used a commercially available Michler's ketone (MK). Michler's ketone was mixed with a chloroform solution of polystyrene (Aldrich chemical) and spin-coated onto another fused silica substrate (Sub-B). The MK concentration in the film was 10% by weight. The Sub-A and -B were fastened together using a vacuum chuck as their coated sides facing each other. They were then exposed to 7 mW/cm² of 365 nm light from an Hg–Xe arc lamp for 3 min. Cinnamate is never directly photo-excited by 365 nm

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