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Infrared Absorption Characteristics of Large-Sized Spherical Aryl-Ether Dendrimers

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A specially designed experimental setup including a newly constructed KBr cell, a light source, a monochromator and an IR detection system suitable for strictly calibrated IR absorption measurements was constructed in order to elucidate strange phenomenon associated with *cis-trans* photo-isomerization at 6.26 μm of the azobenzene core located at the center of an aryl-ether dendrimer (L5AZO). The setup used an ordinary Nichrome source to measure the photon flux, irradiation area, and photon absorption rate as exactly as possible. The photon absorption rate was obtained as 1.2×10^{-3} photons/s-molecule and the absorption cross section of L5AZO molecules was estimated to be 3.1×10^{-19} $\text{cm}^2/\text{molecule}$. Since these values of the absorption rate and absorption cross section are not abnormal, the occurrence of a simultaneous five-photon absorption is almost impossible. Therefore, the five-photon absorption and photo-isomerization shown by L5AZO suggested that the multiphoton process was not simultaneous absorption, but possibly a sequential absorption and energy storage until the equivalent energy of isomerization was reached.

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Introduction

Dendrimers, a type of highly branched polymers, were first synthesized in 1985.¹ They have three-dimensional tree-like structures constructed from repeating monomer units, but are quite different in character from starburst polymers.² The dendrimers are mainly characterized by the numbers of their layered structure, sometimes referred to as "generations", which are composed of monomer units with branching toward the end groups. Their unique structure has led to the realization of some valuable functions, such as modeling photogenic light-harvesting antenna systems,³ molecular capsules,⁴ and shape-designed advanced polymers.^{5,6}

Recently, we found that infrared light ($\lambda = 6.26 \mu\text{m}$, 0.2 eV, $\nu = 1597 \text{ cm}^{-1}$) from an incoherent Nichrome source could induce *cis-trans* isomerization of the azobenzene core located at the center of the aryl-ether dendrimer (L5AZO),⁷ shown in Fig. 1. It is well-known that the *cis-trans* isomerization of azobenzene is induced by visible-light irradiation or heating. It should be impossible to derive the *cis-trans* activation energy of the azo-dendrimer (0.82 eV)⁷ by 6.26 μm radiation. Furthermore, the isomerization reaction rate showed a fifth-order dependence on the photon flux. This means that the isomerization reaction of L5AZO is a five-photon process.⁷ Generally, an incoherent

infrared source cannot induce multiphoton processes. Moreover, it is inconceivable to induce a simultaneous five-photon absorption, even with a high-output laser source. We observed this strange photochemical phenomenon for only large-sized aryl-ether dendrimers having a spherical shape, and found that only 6.26 μm radiation induced the isomerization reaction. To our best knowledge, no report concerning these

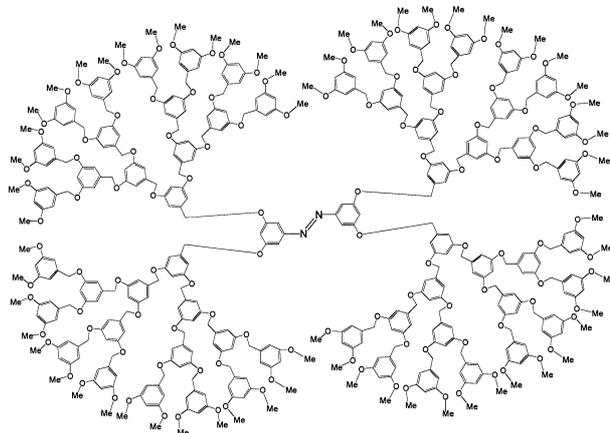


Fig. 1 Structure of *trans*-L5AZO.

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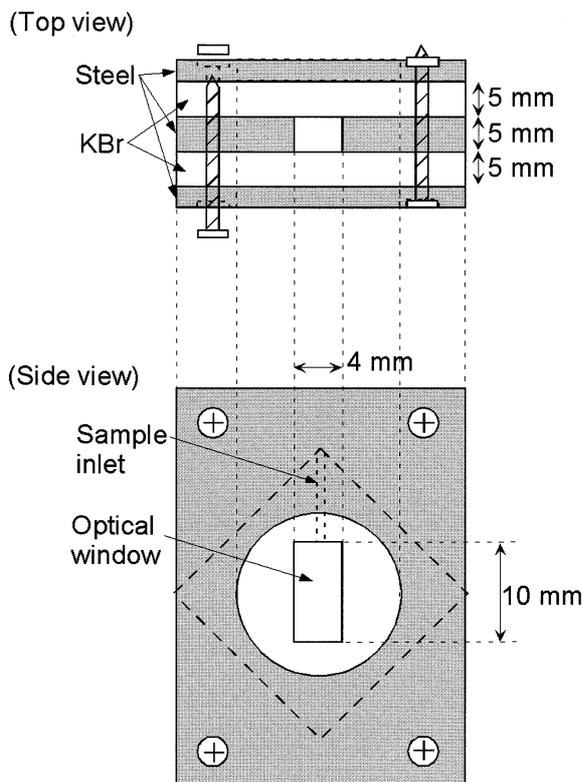


Fig. 2 Schematic illustrations of the KBr cell for absorption measurements.

strange photochemical phenomena has been described concerning any molecules.

Dendrimers are an interesting topic from the viewpoint of not only scientific research, but also of applications.³⁻⁶ A judicious use of dendrimer functions should lead to their utilization in various fields, including spectrophotometric analysis. While recent progress in spectrophotometric analysis has been accelerated by the development of special reagents, such as fluorescent dye molecules, pH indicators, and color indicators, the use of these reagents is restricted mostly to absorption bands in the visible region. The main reason for this seems to be that the production of electronic excited states and the occurrence of chemical reactions are required to contribute to the energy of visible light, *i.e.*, a few eV. If chemical reactions can be effectively induced by IR radiation, the applicability of a spectrophotometric analysis may be expanded into the IR region. The L5AZO molecule, which isomerized by IR radiation, is a possible IR probing reagent. Moreover, the guidelines for molecular design may be provided by the characterization of L5AZO.

In our previous work,⁸ the absorption of 6.26 μm radiation by L5AZO was measured and the absorption cross section was roughly estimated to be $5.5 \times 10^{-17} \text{ cm}^2/\text{molecule}$. Since a conventional KBr cell was used in this study, the sample volume was significantly larger than the IR irradiation volume. Then L5AZO molecules in the irradiation volume could be replaced by those of outside the irradiation volume during the measurements. Thus, the estimated value is still uncertain.

In the present study, we constructed a newly designed KBr cell for which the sample volume matched the irradiation volume, and we measured absorption of L5AZO precisely. The absorption cross section of L5AZO was estimated from the measured absorption.

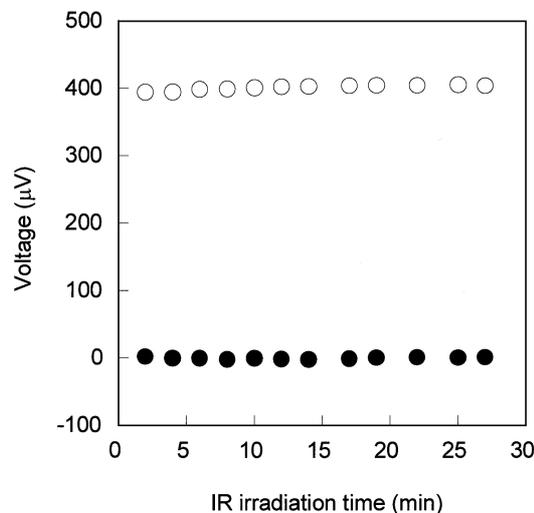


Fig. 3 Time dependence of the voltage detected by the calibrated vacuum thermocouple gauge: L5AZO solution (○), CH_2Cl_2 (solvent) (●).

Experimental

Sample

The L5AZO was synthesized as we previously described.⁷ A $5.5 \times 10^{-5} \text{ M}$ L5AZO solution was prepared using CH_2Cl_2 as a solvent. The sample solution was degassed in freeze-pump-thaw cycles and purged with nitrogen before making measurements at room temperature. The sample of *cis*-L5AZO was prepared by an ultraviolet irradiation (300 W xenon arc light) just before the measurement.

Apparatus

The experimental apparatus for absorption and photon flux measurements has been described in detail previously.⁸ Briefly, a 75-W glow-discharge Nichrome source (Kyocera, SN361, Model NBT-1) was used as an IR light source. White light from the Nichrome source was monochromated to an IR radiation of 6.26 μm (1597 cm^{-1}) by a monochromator (JASCO, Model CT-25T, bandwidth $\pm 50 \text{ cm}^{-1}$). A power of 6.26 μm radiation was monitored with a calibrated vacuum thermocouple gauge (JASCO) for which the DC sensitivity had been corrected by $4.9 \mu\text{V} \cdot \mu\text{W}^{-1} \cdot \text{mm}^{-2}$ and a digital multimeter (Keithley, Model 2010). The absorbance of sample solutions was measured by a conventional spectrophotometer (JASCO, V-570).

KBr cell

For the absorption measurements, we constructed a newly designed KBr cell having a 4 mm \times 10 mm rectangular window, which corresponded to the cross section area of the monochromated 6.26 μm IR light. Matching the sample and irradiation volumes by using this KBr cell eliminated the molecular replacement effect. Figure 2 shows top and side views of the cell. The two frames and spacer were made of stainless steel and had four drilled holes for screws. The optical windows were two KBr plates. The spacer had a 4 mm \times 10 mm rectangular channel and 1 mm diameter sample inlet hole. The five plates were stacked on top of each other and fixed by tightening four screws. To ensure thermal equilibrium of the vacuum thermocouple gauge, all measurements were monitored for 30 min, as shown in Fig. 3.

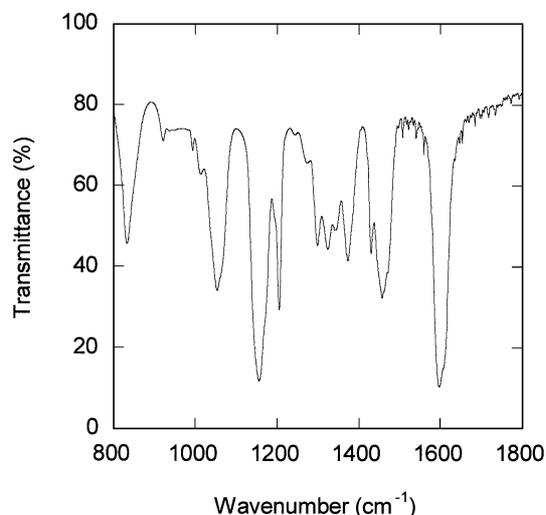


Fig. 4 Typical IR absorption spectrum of L5AZO (KBr pellet).

Results and Discussion

Figure 4 shows a typical IR absorption spectrum of L5AZO in the 800 – 2000 cm^{-1} region. Prominent features in the vicinity of 1597 and 1155 cm^{-1} are a stretching vibrational mode for aromatic rings and a stretching vibrational mode for $\text{CH}_2\text{-O}$, respectively. The bands at 1456 and 1052 cm^{-1} are a scissoring mode for CH_2 and a stretching vibrational mode for C-O , respectively. Only the absorption band at 1597 cm^{-1} , that is 6.26 μm , appears to indicate a strange phenomenon.

In order to confirm the *cis-to-trans* isomerization of L5AZO by 6.26 μm radiation, we measured the IR irradiation-time dependence of the absorbance of the sample solution at 340 nm. Since the absorption band at 340 nm is characteristic of *trans*-L5AZO, the *cis-to-trans* isomerization can be confirmed by monitoring the increase of the absorbance at 340 nm. The results are shown in Fig. 5. We can confirm the *cis-to-trans* isomerization of L5AZO by 6.26 μm radiation under the present experimental conditions.

The number of photons absorbed by L5AZO in CH_2Cl_2 was measured precisely as in our previous work under the same experimental conditions. The photon fluxes of 6.26 μm after passing through a *cis*-L5AZO solution and a pure solvent (CH_2Cl_2) were measured, and the net absorption photon rate by *cis*-L5AZO was calculated. The photon flux from the Nichrome source was obtained as a DC voltage that was detected by the calibrated IR detector.

The total energy flows which transmitted the solvent and L5AZO solution were obtained as $E_{\text{CH}_2\text{Cl}_2}$ (W) and E_{Solution} (W), respectively. Here, the photon flux passing through the solvent was assumed to be an effective photon flux for L5AZO absorption, ϕ_E (photons/s $\cdot\text{cm}^2$). Namely,

$$\phi_E = \frac{E_{\text{CH}_2\text{Cl}_2}}{h\nu} \times \frac{1}{S}, \quad (1)$$

where $h\nu$ is the energy of a photon with a wavelength of 6.26 μm and S is the irradiation area, 0.4 cm^2 . The net absorption energy by L5AZO, E_{L5AZO} , was expressed as

$$E_{\text{L5AZO}} = E_{\text{CH}_2\text{Cl}_2} - E_{\text{Solution}} \quad (2)$$

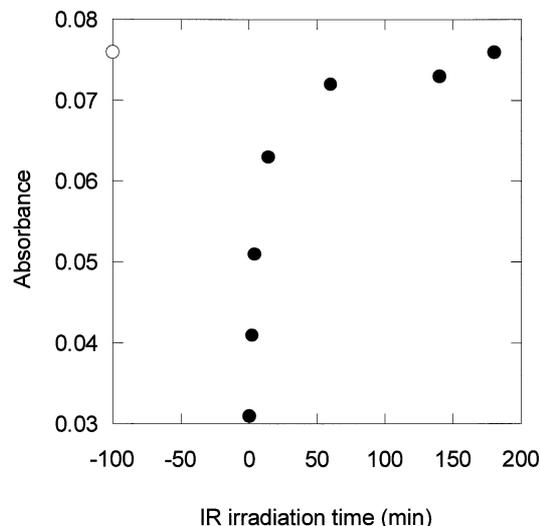


Fig. 5 IR irradiation-time dependence of the absorbance of the L5AZO solution at 340 nm. The open circle is the absorbance for *trans*-L5AZO. The black circles are the absorbance for *cis*-L5AZO during IR irradiation after UV radiation.

Table 1 Spectroscopic data of L5AZO for 6.26 μm IR radiation

$E_{\text{CH}_2\text{Cl}_2}$	4.9×10^{-4}	W
E_{L5AZO}	2.5×10^{-7}	W
ϕ_E	3.8×10^{15}	photons/s $\cdot\text{cm}^2$
n_{L5AZO}	1.2×10^{-3}	photons/s $\cdot\text{molecule}$
σ	3.1×10^{-19}	$\text{cm}^2/\text{molecule}$

The absorption rate by L5AZO, n_{L5AZO} (photons/s), is expressed as

$$n_{\text{L5AZO}} = \frac{E_{\text{L5AZO}}}{h\nu} \times \frac{1}{N} = \phi_E \sigma, \quad (3)$$

where N is the number of L5AZO molecules in the irradiation volume, $V = 0.2 \text{ cm}^3$, and σ is the absorption cross section of L5AZO for 6.26 μm radiation. The obtained values are summarized in Table 1. If the five 6.26 μm photons were absorbed simultaneously, the obtained absorption cross section should be extraordinarily large. As shown in Table 1, the absorption cross section of L5AZO was not very large and was on the same order as other phenyl-containing substances. Therefore, we concluded that the L5AZO molecule did not absorb five photons simultaneously, but rather sequentially. In this case, we should assume intramolecular storage of the photon energy, because the photon energy was consumed in the *cis-to-trans* isomerization simultaneously. Since the activation energy of the isomerization of an azobenzene group (0.82 eV) is nearly equivalent to the five-photon energy, the phenomenon seemed to be a non-dissipative system.

Then, we assumed a new model for the five-photon-induced isomerization. In this model, the photon energy absorbed is stored in the L5AZO molecule for a long time, to await the fifth absorption event. After that, the energy is transferred to the core unit (azobenzene) without dissipation, and is consumed simultaneously by an isomerization reaction. Moreover, this strange photochemical phenomenon may be related to the structure of dendrimers, since the isomerization was observed in

only large-sized aryl-ether dendrimers having a spherical shape. In order to verify the validity of the model experimentally, a study along these lines is in progress in our laboratory. These results will be reported in the near future.⁹ If the photo-mechanisms of L5AZO are solved in detail, this information should provide guidelines for the molecular design of IR probing molecules.

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