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Photoisomerization in dendrimers by harvesting of low-energy photons

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Infrared radiation can induce low-frequency molecular vibrations, but, with the exception of hydrogen-bond reorganization[1–3], the excitation energy tends to be dissipated rapidly through molecular collisions rather than inducing photochemical changes. Here we show that in a macromolecular system that is designed to be insulated against collisional energy scattering, infrared absorption can excite photoisomerization by multiphoton intramolecular energy transfer. We have prepared highly branched dendrimers[4–6] from aryl ethers with a photoisomerizable azobenzene core, in which infrared excitation of the aromatic units is apparently followed by a channelling of the absorbed energy to the core while the dendrimer matrix protects against collisional de-excitation. These findings suggest a strategy for harvesting low-energy photons to effect chemical transformations.

Dendrimers are nanometre-size macromolecules with a regular tree-like array of branch units[4–6]. We have recently synthesized dendrimer porphyrins in which a porphyrin chromophore is spatially isolated by the dendrimer framework[7–10]. As may be expected from the gradient in branch density from the interior to the exterior, the surface of these large dendrimers is conformationally frozen, whereas the interior space is not constrained irrespective of the size of the dendrimer framework, so that the core porphyrin is able to undergo free conformational motion[8]. Thus spherical, large dendrimers should provide a non-constrained environment insulated from collisional energy scattering. This motivated us to explore the possibility of intramolecular energy transfer within these unimolecular matrices.

For this purpose, we have synthesized a series of azobenzene-containing aryl ether dendrimers (*trans*-LnAZO, where n is the number of aromatic layers and is 1, 3, 4 or 5; Fig. 1), by alkaline-mediated coupling of dendritic benzyl bromides (L(n − 1)Br; ref. 8) with *trans*-3,3′,5,5′-tetrahydroxyazobenzene. We characterized this series of *trans*-LnAZO compounds unambiguously, by using ^{1}H NMR, ultraviolet–visible spectroscopy and matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (further details are available; see Supplementary Information). Azobenzenes are photochromic molecules that isomerize from *trans* to *cis* on ultraviolet irradiation, and from *cis* to *trans* either thermally or on exposure to visible light[11]. Single-photon (ultraviolet) photoisomerization of azobenzene dendrimers similar to ours was demonstrated recently[12].
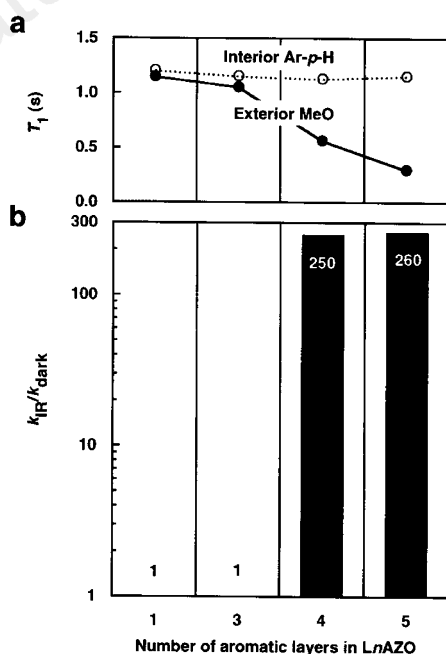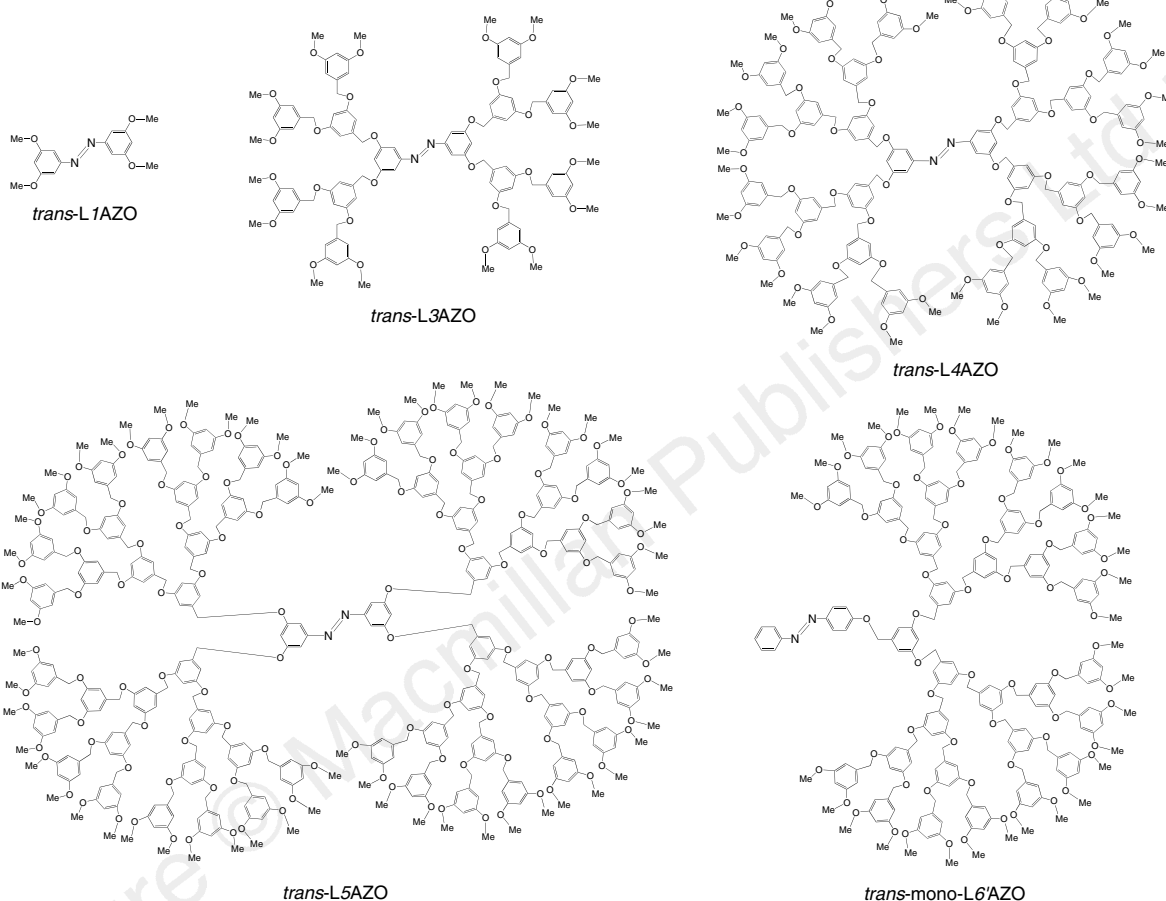
We measured ^{1}H NMR pulse relaxation times (T_1) of the *trans*-LnAZO family at 21 °C in CDCl$_3$, and confirmed an egg-like structural resemblance[8] to higher-generation *trans*-LnAZOs. The T_1 value for the methoxy protons on the exterior surface (filled circles in Fig. 2a) decreased sharply as the dendrimer framework became larger whereas that of the protons in the interior azobenzene functionality (open circles in Fig. 2a) remained almost intact. Thus L4AZO and L5AZO possess a non-constrained interior environment within a stiff exterior shell.

On ultraviolet radiation at 21 °C in CHCl$_3$, *trans*-LnAZO (n = 1, 3–5, 5 × 10^{-5} M) isomerized normally to *cis*-LnAZO, which then gradually isomerized back to the *trans* form after the irradiation was stopped. When a CHCl$_3$ solution of *cis*-L5AZO in a KBr cell was exposed to infrared radiation (a 75-W glowing nichrome source) in an infrared spectrophotometer, it isomerized very rapidly to *trans*-L5AZO. We found that this infrared-radiation-induced isomerization depends greatly on the size of the dendrimer framework (Fig. 2b): on exposure to the infrared radiation *cis*-L5AZO completely isomerized to the *trans* form in only 8 min (Fig. 3b) at a rate constant of 3.4 × 10^{-3} s^{-1}, which is 260 times as high as that of the thermal isomerization at 21 °C in the dark (1.3 × 10^{-5} s^{-1}, Fig. 2b) and even 23 times as high as the rate constant found on irradiation with visible light (440 ± 9 nm, 21 °C). Similarly, under infrared illumination *cis*-L4AZO underwent rapid isomerization to *trans*-L4AZO (Fig. 2b). In sharp contrast, we observed no effect of infrared radiation for the isomerization of the smaller homologues *cis*-L1AZO (Fig. 3a) and *cis*-L3AZO. *cis*-L1AZO was also unaffected by the infrared radiation even in the presence of a large dendritic benzyl alcohol (L5OH; 4 equiv.) unanchored to the azobenzene unit. Furthermore, although the molecular weight is almost comparable to that of L4AZO, the isomerization of *cis*-mono-L6′AZO (Fig. 1), a non-spherical mono-dendritic azobenzene, was not facilitated by infrared. Thus spatial isolation of the azobenzene functionality by the highly constrained, large dendrimer matrix (Fig. 2a) seems to be a prerequisite for the infrared-radiation-induced isomerization.

We further investigated the isomerization of *cis*-L5AZO (5 × 10^{-5} M, in CHCl$_3$ at 21 °C) by using monochromatized infrared radiation (a 75-W glowing nichrome source through a JASCO model CT-25C monochromator, bandwidth ±50 cm^{-1}) of three different wavenumbers; 2,500 cm^{-1} (transparent for LnAZO), 1,597 cm^{-1} (a stretching vibrational band for aromatic rings) and 1,155 cm^{-1} (a stretching vibrational band for CH$_2$–O), and found that only the 1,597 cm^{-1} radiation facilitates the isomerization reaction. This observation indicates that the infrared energy absorbed by the aromatic rings excites the *cis*-to-*trans* isomerization. We consider the following two possibilities for the mechanism of this effect; (1) direct infrared excitation of the interior azobenzene moiety, and (2) intramolecular energy transfer from the dendrimer matrix to the azobenzene. To investigate (2), we selectively excited the dendrimer framework of *cis*-LnAZO at its characteristic 280-nm absorption, where we again observed a definite
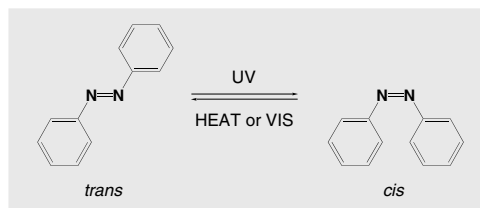
Figure 1 Schematic representations of the isomerization of azobenzene (top left) and the structures of *trans*-LnAZO ($n = 1, 3$–5) and *trans*-mono-L6'AZO; here n represents the number of aromatic layers. In the equation at top left, *UV* indicates ultraviolet radiation and *VIS* indicates visible light radiation.

Figure 2 Effect of the number of aromatic layers (n) in LnAZO on: **a**, ^{1}H NMR pulse relaxation times (T_1) of *trans*-LnAZO ($n = 1, 3$–5) at 21 °C; **b**, first-order rate constants of the *cis*-to-*trans* isomerization of LnAZO ($n = 1, 3$–5) at 21 °C under infrared irradiation (k_{IR}) relative to those of the thermal isomerization in the dark (k_{dark}). The experimental procedures for **b** are described in the Methods section.
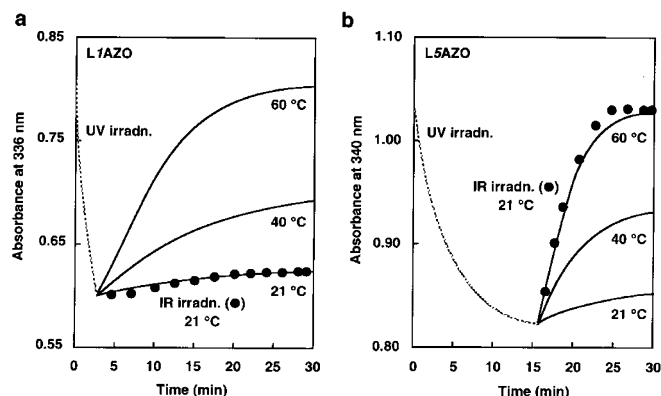
Figure 3 Isomerization profiles of L1AZO (**a**) and L5AZO (**b**) in infrared radiation (●) at 21 °C in comparison with the thermal isomerization profiles (solid lines) at 21, 40 and 60 °C in the dark. Experimental details are given in the Methods section.
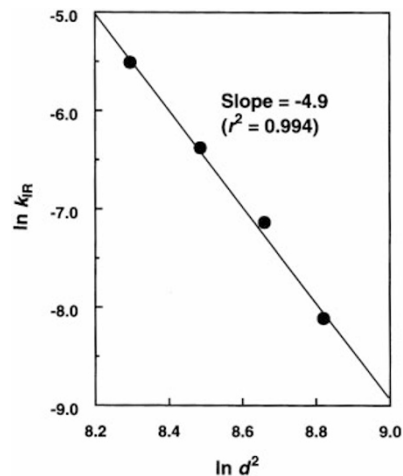

Figure 4 Dependence on the irradiation distance d of the first-order isomerization rate constant (k_{IR}) of *cis*-L5AZO when exposed to infrared radiation. A $CHCl_3$ solution of *cis*-L5AZO (5×10^{-5} M) in a KBr cell of 5-mm path length was exposed at 21 °C to infrared radiation (a 75-W glowing nichrome point source) at four different distances (63.3, 69.6, 76.0 and 82.3 mm); the rate constants (k) were obtained as given in the Methods section.

acceleration of the *cis*-to-*trans* isomerization for L4AZO and L5AZO, but not for L1AZO, L3AZO and mono-L6′AZO (further details are available; see Supplementary Information). In every case, the fluorescence from the dendrimer framework (310 nm) was not quenched at all. Considering a possible internal conversion via the singlet excited state to vibrational modes of the ground state; the correlation of the observed results on 280-nm excitation with those in Fig. 2b indicates that the infrared-radiation-induced isomerization of L*n*AZO involves a contribution of the matrix-to-core intramolecular energy transfer. We therefore conclude that the large dendrimer matrix here does not simply serve to insulate the interior units from collisional energy scattering, but it also functions as an efficient photon-harvesting antenna.

For comparison, we investigated thermal isomerization of *cis*-L5AZO at three different temperatures (Fig. 3b) and found that the rate of isomerization on infrared excitation is almost comparable to that of the thermal isomerization at 60 °C. From the data shown in Fig. 3b, the activation free energy ($\Delta G^{\ddagger}$) at 21 °C for the thermal isomerization of *cis*-L5AZO was found to be 19.4 kcal mol^{-1} (0.84 eV). We further investigated the effect of different photon fluxes on the infrared-radiation-induced isomerization of *cis*-L5AZO by changing the distance d of the sample from a point light source; the photon flux applied to the sample is in inverse proportion to d^2. The observed dependence of the isomerization rate constant (k_{IR}) on d^2 (Fig. 4) indicates that 4.9 photons (0.98 eV at 1,597 cm^{-1}) are involved in this photochemical process. L5AZO bears 62 aromatic groups, and may possibly absorb several photons simultaneously even in such a low photon flux field.

There is much interest in the design of molecular systems for light harvesting and efficient conversion of photons into chemical energy[13–16]. Our results suggest a new strategy for using low-energy photons for chemical transformations, and the possibility of using dendrimers as tunable light-harvesting matrices. □

Methods

A $CHCl_3$ solution of *trans*-L*n*AZO (5×10^{-5} M), in a quartz cell of 10-mm path length connected to a 10-ml round-bottomed flask with a three-way stopcock, was irradiated by a 300-W xenon arc light through a band pass filter (340 ± 9 nm) to induce the *trans*-to-*cis* isomerization (broken lines). After the spectral change subsided, the irradiated solution was transferred to a KBr cell of

5-mm path length and exposed at 21 °C to infrared radiation (a 75-W glowing nichrome source) in an infrared spectrophotometer (JASCO FT-IR model 5300), where the temperature increase was only within 1 °C, as observed by a thermocouple microdetector. The entire solution was periodically transferred to a quartz cell of 10-mm path length and the electronic absorption spectrum was taken, to follow the *cis*-to-*trans* isomerization. For thermal isomerization, the quartz cell, containing the irradiated solution at 340 ± 9 nm, was set in a ultraviolet–visible spectrophotometer equipped with a temperature controller, and the absorbance at 336 nm (for L1AZO) or 340 nm (for L5AZO) was continuously monitored at a designated temperature.

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