# Photochromism of 36-Armed Liquid Crystalline Dendrimer

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**Abstract:** The photochromism of a 36-armed liquid crystalline dendrimer **D6** was briefly described in this paper.    The molar absorption coefficient, photoisomerization and photo back-isomerization of **D6** in solution were investigated by UV/Vis absorption spectra.    The results indicate that the photochromism and photo back-isomerization of **D6** in chloroform ($CHCl_3$) and tetrahydrofuran (THF) solutions are in accordance with the first order kinetics.    The photochromism rate constants of **D6** are $10^{-1}$ $s^{-1}$, it is $10^7$ times larger than that of side-chain liquid crystalline polymers containing the same azobenzene moieties.

**Keywords:** Photochromism, liquid crystalline dendrimer, photo back-isomerization.

Over the past few years there has been intense interest in the unique properties exhibited by dendrimers with a regular treelike array of branching units[1-5].    Quite recently, dendrimers with different designed functionalities have become hotspots of academic and practical interest[6-10].    We have successfully carried out the molecular design and got a series of liquid crystalline carbosilane dendrimers with 4, 12 and 36 arms in the periphery[11-13].    The 36-armed liquid crystalline dendrimer **D6** showed nematic phase and its phase behaviour was Cr90N105I113N75Cr[13].    The structures of **D6** and mesogenic unit **M6** were shown in **Figure 1**, and the dendritic compound showed simultaneously liquid crystalline and photochromic properties.    The photochromism of **D6** was briefly studied by the UV/Vis absorption spectrum in this paper.

The photoirradiation was carried out by a 200W high-pressure Hg-Xe lamp (Oriel) equipped with a glass filter and HP8451A UV/Vis spectrophotometer for ultraviolet irradiation.    A series of different concentration solutions of **D6** in chloroform ($CHCl_3$) and tetrahydrofuran (THF) were prepared, they were scanned in the range of 300-600 nm [14].    The solutions were immediately subjected to UV/Vis absorption measurement and absorbance at $\lambda_{max}$=360 nm of each solution was recorded with time.    Draw the absorbency of $\lambda_{max}$ with the corresponding concentration, all the graphs gave straight line. The slope of the line is the molar absorption coefficient $\varepsilon$ of **D6** and its $\varepsilon$ in $CHCl_3$ and THF were $1.13\times10^6$ and $1.06\times10^6$ ($L\cdot mol^{-1}\cdot cm^{-1}$), respectively.    They are about 35 times higher than that of **M6**.    So the absorption of **D6** is stronger than the mesogenic

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**Figure 1**    The structures of liquid crystalline dendrimer **D6** and mesogenic unit **M6**



$$\boxed{\phantom{x}}\!\!\!\!\!\!\!\rangle = C_6H_{13}O\!-\!\bigcirc\!-\!N{=}N\!-\!\bigcirc\!-$$
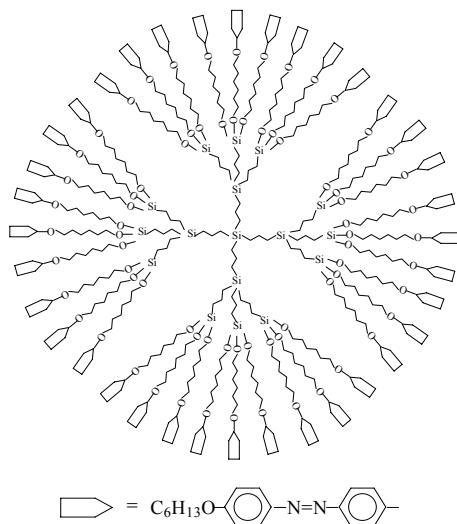
unit's due to it has more azobenzene number.

　　The solutions of **D6** in CHCl$_3$ and THF were irradiated by ultraviolet light at room temperature.    The absorptions were recorded at different time intervals until spectral variation was no longer evident.    As shown in **Figure 2**, in the case of irradiation of the solution markable spectral changes were observed.    We observed dramatic decrease in the optical density in the spectral region corresponding to the $\pi$-$\pi$* transition with the maximum at 360 nm, whereas in the region of the n-$\pi$* transition (near 450 nm) a slight increase in absorbance was observed.    The occurrence of two distinct isobestic points at 426 and 324 nm as well as the similarity of the UV spectra of the irradiated samples at the photostationary state with that of *cis*-azobenzene indicated that only two absorbing species (*trans* and *cis* isomers) were present and no side reactions such as photocrosslinking or photodegradation occured.    Furthermore, the presence of two isobestic points (at 324 and 426 nm) during reversible isomerization processes clearly indicated the effective and reversible conversion of the azo unit.

　　In all cases $\ln[(A_0\text{-}A_\infty)/(A_t\text{-}A_\infty)]$, where $A_0$, $A_t$ and $A_\infty$ are the absorbances at 360 nm at zero time, t and infinite time, respectively, it has a linear dependence on the irradiation time (see **Figure 3**).    They were in accordance with the first order kinetics and the slope is the photochromism rate constant $k_p$.    $k_p$ of **D6** in CHCl$_3$ and THF were 0.416 and 0.346 (s$^{-1}$), respectively.    They were very similar and of the same order of magnitude as those observed for the low molecular weight **M6**[14], at the same time they were 10$^7$ times larger than those of side-chain liquid crystalline polymers containing the same azobenzene moieties in the corresponding solutions[15-16].    These results indicated that the dendritic structure did not significantly affect the photoisomerization rate, probably due to the presence of the flexible hexamethyl spacers.    Because there were no entanglements and bondage between the main chain and the side chains in the dendritic molecule, the liquid crystalline dendrimer **D6** has better photochromism and

photoresponse behaviour than the common liquid crystalline polymers.

It is well known that azobenzene-type compounds undergo an efficient and fully reversible photoisomerization reaction.  If the compound in solution situation, the process of *trans-cis* isomerization is photochemically reversible; that is, under the action
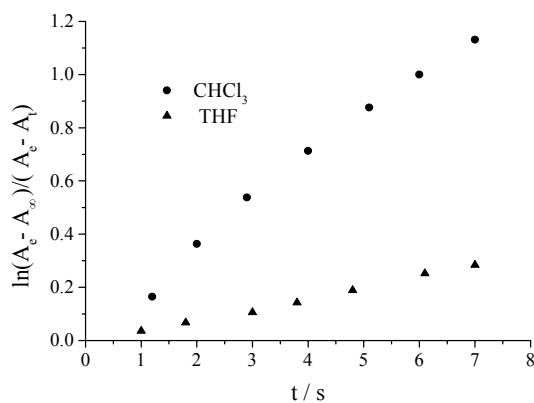
**Figure 2**    UV/Vis spectrum of **D6** in tetrahydrofuran solution
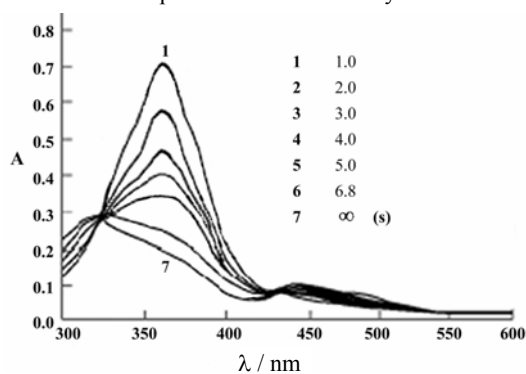


**Figure 3**    Photoisomerization of **D6** in solutions
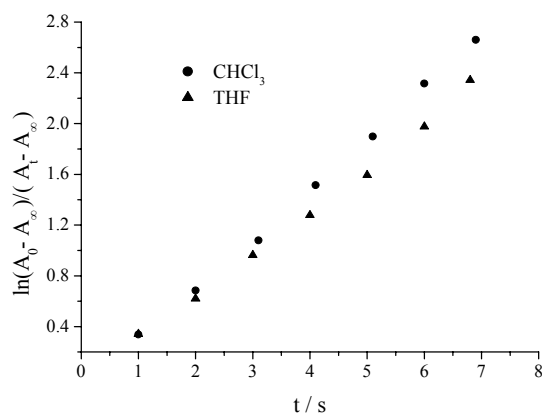


**Figure 4**    Photo back-isomerization of **D6** in solutions

of visible light, back *cis-trans* isomerization takes place.   The solutions of **D6** were irradiated by the 360 nm UV light for enough time (5 min) and then immediately subjected to the 470 nm visible light, then the absorbance at different time was recorded to study the process and the kinetics of the photo back-isomerization.

In the formula $\ln[(A_e-A_\infty)/(A_e-A_t)]=(A_0-A_\infty)/(A_e-A_\infty)\cdot k_t\cdot t$, $A_0$ is the absorbance at $\lambda_{max}$ at zero time, and $A_\infty$ is the absorbance after 5 min (t=∞) irradiation at $\lambda_{max}$ that can be regarded as the absorbance of the photostationary state.   Then $A_t$ and $A_e$ are the absorbances at 470 nm at t time and infinite, which $A_e$ is the absorbance of the equilibrium state of photo back-isomerization.   $k_t$ is rate constant of the *cis-trans* isomers reaction during the photo back-isomerization under the irradiation at 470 nm visible light.   To calculate the rate of this process, the values of $\ln[(A_e-A_\infty)/(A_e-A_t)]$ were plotted *versus* the time.   We get the rate constant $k_t$ from the slope of the line (see **Figure 4**).   They are in accordance with the first order kinetics and the values of $k_t$ in $CHCl_3$ and THF are 0.128 and 0.0177 ($s^{-1}$), respectively.   They are of the same order of magnitude as those observed for **M6**[14], it shows that the **D6** has better photo-reversibility. So the liquid crystalline dendrimer has potential applications and can be expected to be a new type photocontrolable switch and functional information material.

## Acknowledgment

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