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The photochemical isomerization of cross-linked 1,3,5-tristyrylbenzene dendrimer with hula-twist mechanism

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Abstract—A cross-linked 1,3,5-tristyrylbenzene dendrimer **5** was synthesized to study the photochemical isomerization mechanism. On irradiation, **5** isomerized with the quantum yields ($\Phi_{E\rightarrow Z}$) of 0.063, which was not very much different from that for a model compound **1** ($\Phi_{E\rightarrow Z}$ 0.080), supporting a volume-conserving hula-twist (HT) mechanism during the photochemical *E*–*Z* isomerization.

Photoisomerization of small molecules has been widely studied and the isomerization mechanism in the excited state has been revealed.[1,2] For *E*–*Z* photoisomerization of C=C double bond, one bond flip (OBF), and hula-twist (HT) mechanisms have been proposed. In the conventional OBF motion, the one half of the molecule turns over through the perpendicular intermediate. The HT mechanism, proposed by Liu and Asato in 1985, is the simultaneous isomerization of C=C double bond and adjacent single bond.[3] Since the HT pathway needs much less reaction volume than OBF process, it can be used to explain how the retinal is able to undergo rapid photoisomerization in confined media[4] or how a small molecule isomerize in organic glass at −196 °C.[5] In the photoisomerization of the dendritic stilbenoid compounds,[6–8] we have found experimental support of rapid photoisomerization through the HT pathway, followed by slow conformational change of the dendritic substituents.[9]

In this communication, we report comparison of *Z*- to *E*-isomerization efficiency for a cross-linked 1,3,5-tristyrylbenzene dendrimer **5** and its model compound **1**[8] in THF solution. Whereas only the HT mechanism allows **5** to isomerize, compound **1** can undergo photoisomerization with both the OBF and the HT mechanisms.

As shown in Scheme 1, compound **2** was prepared by the deprotection of **1** with BBr_3 in dichloromethane. Dendron **3** was prepared from the corresponding alcohol, which has been reported by Zimmerman et al.[10] Tristyrylbenzene dendrimer **4** was then obtained by coupling reaction of **2** and **3** in the presence of K_2CO_3 and 18-crown-6 ether in butanone, followed by cross-linking reaction with Grubb's ruthenium catalyst[11,12] in benzene to give the cross-linked tristyrylbenzene dendrimer *E*,*E*,*E*-**5**.[13] After purification by flash column chromatography and by GPC, the MALDI-TOF mass spectra showed peaks for 12 fully cross-linked dendrimer *E*,*E*,*E*-**5** and for 11- and 10-cross-links. The ratio of the mass peak intensity is 1.0:3.9:2.9 for 12-, 11-, and 10-cross-links, respectively. All the ^{1}H NMR signals of *E*,*E*,*E*-**5** were broaden because of the existence of 10- and 11-cross-linked dendrimers. Since the cross-linking reaction with Grubb's catalyst can take place not only between two adjacent alkenes but also proceeds alternately,[10] the 11- and 10-cross-linked dendrimers were produced and were not separable by silica gel column chromatography or by GPC. The reaction could not be completed even when the reaction time was extended.

Figure 1 shows the change in the absorption spectra of **1** and *E*,*E*,*E*-**5** upon the UV irradiation at 330 nm. The absorption spectra of **1** and *E*,*E*,*E*-**5** before irradiation were similar except around 280 nm, which is attributed to the peripheral dendrons. The spectral change of both **1** and **5** were also very similar in the region at 300–400 nm. On UV irradiation at 330 nm, **1** in THF at

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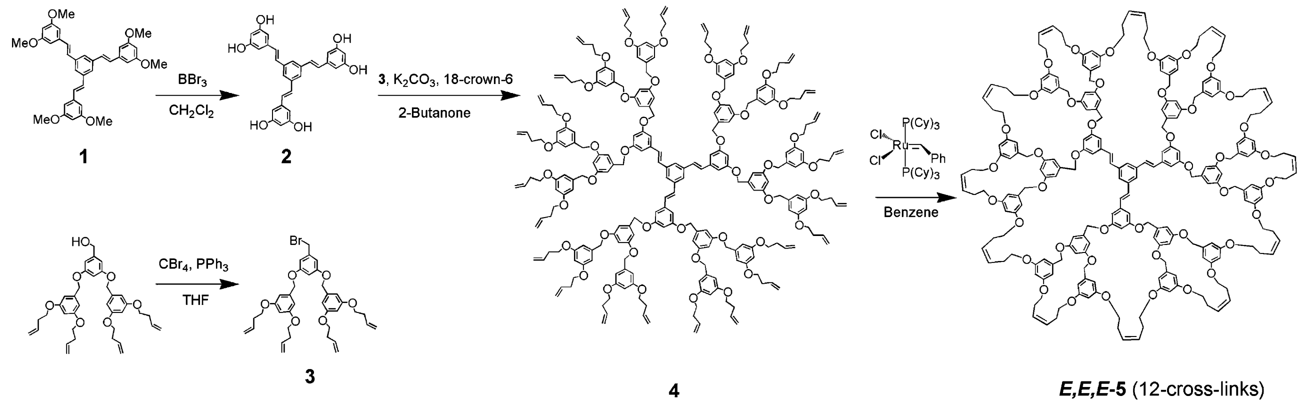

Scheme 1. Synthesis of cross-linked dendrimer *E*,*E*,*E*-**5**.

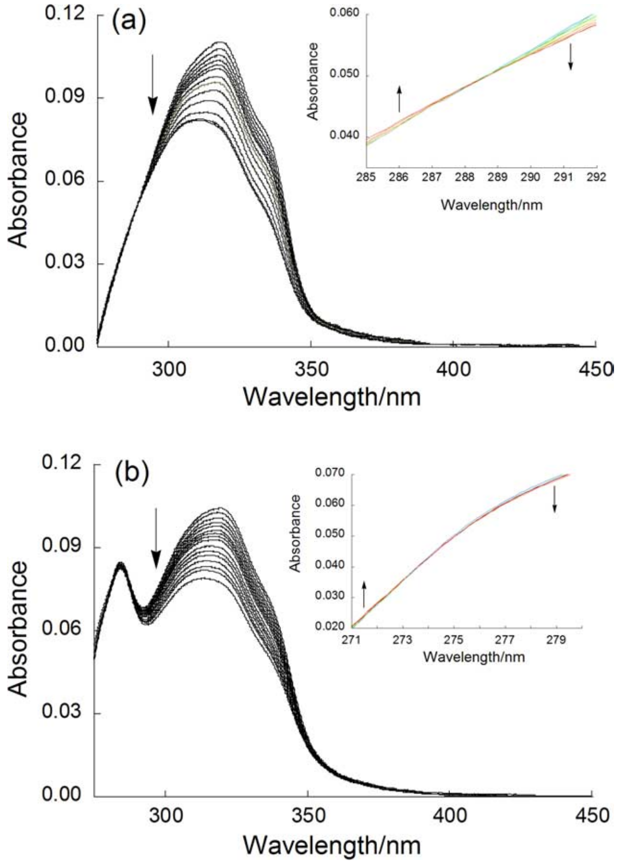

Figure 1. (a) Change in the absorption spectra of **1** upon the irradiation at 330 nm light from a 150 W Xenon lamp through a monochrometer in THF under argon. (b) Change in the absorption spectra of cross-linked dendrimer **5** in the same conditions.

room temperature under argon underwent mutual photochemical isomerization only between *E*,*E*,*E*- and *Z*,*E*,*E*-isomers.[8,14] As shown in the inset in Figure 1a, the isosbestic point at 288 nm can be observed during the irradiation, supporting that the isomerization takes place between *E*,*E*,*E*- and *Z*,*E*,*E*-isomer. The isosbestic point for **5** during the photoirradiation was found at 273 nm (inset in Fig. 1b), which it is not very clear because the absorbance around 272–275 nm for both *E*,*E*,*E*-**5** and its photoproduct are almost identical. However, it can be considered that the photochemical isomerization only between *E*,*E*,*E*-**5** and *Z*,*E*,*E*-**5** takes place at least in this conditions, due to the similar spectral change of **1** and **5**.[15] The irradiated sample of **5** was the mixture of 12-, 11-, and 10-cross-linked dendrimers. Therefore, the isosbestic point for irradiation of **5** indicates that the absorption spectra of *E*,*E*,*E*- as well as *Z*,*E*,*E*-isomers of 12-, 11-, and 10-cross-links are very similar to each other.

The corresponding time profiles for the absorbance change during the photoirradiation of **1** and **5** monitored at 330 nm are shown in Figure 2a. In the same irradiation conditions, the decrease of the absorbance for the cross-linked dendrimer **5** was slower than that for compound **1**, probably because the isomerization with OBF mechanism is impossible in **5**. Previously, we have determined the quantum yield for the photochemical $E,E,E \rightarrow Z,E,E$ isomerization of **1** in the same conditions ($\Phi_{E\rightarrow Z}$ 0.080).[8,16] The initial changes in the absorbance at 330 nm of **1** and **5**, as shown in Figure 2b, were compared to give the quantum yield for the photochemical isomerization of **5** ($\Phi_{E\rightarrow Z}$ 0.063).

The obtained similar spectral change for **5** to that for **1** in the same condition indicates that the isomerization of **5** takes place only between *E*,*E*,*E*- and *Z*,*E*,*E*-isomers probably with HT mechanism (Fig. 3). Although **5** can take only HT pathway, the $\Phi_{E\rightarrow Z}$ value for **5** was not very different from that for **1**. Since HT demands at least small conformational change, the interior of the cross-linked dendrimer should be flexible enough to allow the core unit can smoothly undergo the isomerization with HT process. Meanwhile, there are theoretical reports where OBF and HT can be the competing relaxation processes of the excited Frank–Condon species.[17,18] Although it is considered that OBF is favored in solution and HT is favored in confined media,[4,19] the isomerization of **1** in solution at room temperature may take place not only by OBF, but also by HT mechanism. A recent paper by Fuß et al., who concluded that HT can take place even in small molecules such as stilbene without any substituents in gas phase, since HT motion does not need any external constraint but is driven by an internal force, which is the slope on the way through a conical intersection (CI).[20]

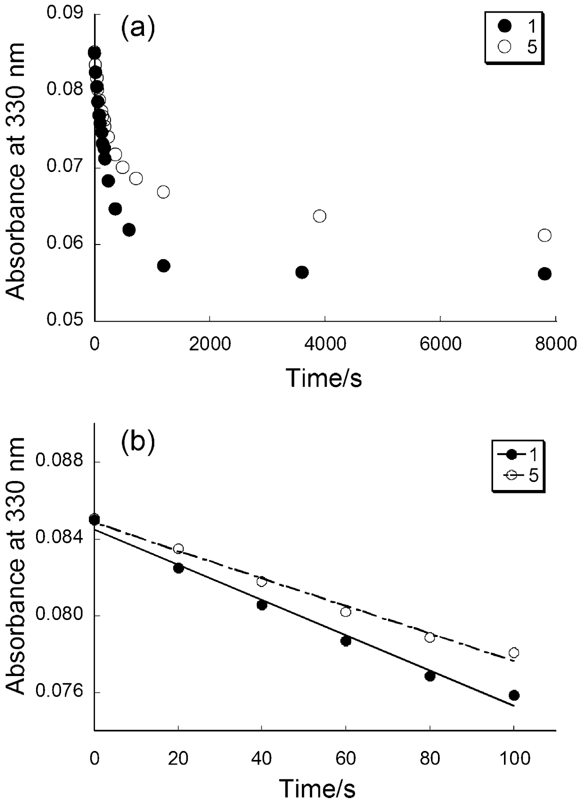

Figure 2. (a) Time dependence of the absorbance of **1** and **5** observed at 330 nm upon the irradiation at 330 nm light in THF at room temperature. (b) Initial change of the absorbance of **1** and **5** observed at 330 nm.

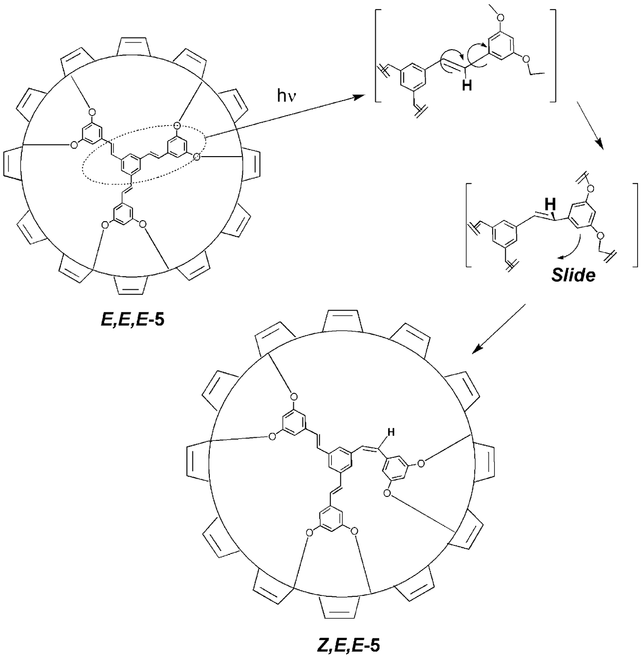

Figure 3. Schematic drawing of photochemical *E,E,E* → *Z,E,E* isomerization of **5** with the hula-twist (HT) mechanism.

In conclusion, we showed the clear support of HT mechanism during the photochemical *E–Z* isomerization in a cross-linked tristyrylbenzene dendrimer.

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13. Compound **3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (2H, d, $J = 2.2$ Hz, ArH), 6.56 (4H, d, $J = 2.2$ Hz, ArH), 6.53 (1H, t, $J = 2.2$ Hz, ArH), 6.41 (2H, t, $J = 2.2$ Hz, ArH), 5.80–6.00 (4H, m, $CH_2{=}C\mathit{H}$), 5.08–5.18 (8H, m, $C\mathit{H}_2{=}CH$), 4.93 (4H, s, $ArOC\mathit{H}_2Ar$), 4.39 (2H, s, CH_2Br), 3.99 (8H, t, $J = 7.0$ Hz, $ArOC\mathit{H}_2$), 2.48–2.58 (8H, m, CH_2). Compound **4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (3H, s, ArH), 7.13 (6H, s, CH=CH), 6.39–6.73 (63H, m, ArH), 5.82–5.89 (24H, m, $CH_2{=}C\mathit{H}$), 5.05–5.15 (48H, m, $C\mathit{H}_2{=}CH$), 4.90–4.99 (36H, m, $ArC\mathit{H}_2OAr$), 3.90–3.99 (48H, m, $RC\mathit{H}_2OAr$), 2.24–2.50 (48H, m, $C\mathit{H}_2$). MALDI-TOFMS: calcd for $C_{252}H_{276}O_{42}Na$ $[M+Na]^+$: *m/z* 3993.9. Found: 3996.9. Compound **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (3H, br s), 7.13 (6H, br s), 6.30–6.70 (63H, m), 5.50–5.89 (24H, m), 4.90–5.18 (36H, m), 3.95 (48H, br s), 2.47 (48H, br s). MALDI-TOFMS calcd for $C_{228}H_{228}O_{42}Na$ $[M+Na]^+$ (12-cross-links): *m/z* 3660.6. Found: 3664.8. $C_{230}H_{232}O_{42}Na$ $[M+Na]^+$ (11-cross-links): *m/z* 3691.2. Found: 3691.8. $C_{232}H_{236}O_{42}Na$ $[M+Na]^+$ (10-cross-links): *m/z* 3719.3. Found: 3719.8.
14. In ^{1}H NMR spectrum of the irradiated sample of compound **1**, only *Z,E,E*-isomer was observed as a single product. For example, the singlet peak δ 7.14 (6H, s, *trans*-CH=CH–) of compound **1** changed only to three peaks after irradiation: δ 7.04 (2H, d, $J = 16$ Hz, *E*-CH=CH), 6.91 (2H, d, $J = 16$ Hz, *E*-CH=CH), and 6.62 (2H, s, *Z*-CH=CH).

15. *E*,*E*,*E*-**1** underwent photochemical isomerization to *Z*,*E*,*E*-**1** giving a mixture of *E*,*E*,*E*- and *Z*,*E*,*E*-**1** at the photostationary state at room temperature under argon atmosphere, as observed by ^{1}H NMR spectroscopy of olefin protons.[14] Thus, *Z*,*E*,*E*-**1** undergoes photochemical isomerization to *E*,*E*,*E*-**1** at room temperature. *Z*,*Z*,*E*-Isomer of **1** could be obtained when the photochemical isomerization was carried out at high temperature (at 50 °C) or under oxygen atmosphere. The study on the detail of the isomerization including *Z*,*Z*,*E*-isomer is on going.
16. Quantum yield of $E,E,E \rightarrow Z,E,E$ isomerization of **1** in THF was determined on irradiation at 330 nm from a 150 W xenon lamp through a monochrometer. The sample solution was deaerated by bubbling argon and was irradiated to keep the conversion within 8%. The light intensity was determined by tris(oxalato)ferrate(III) actinometry. The concentration of each isomer in THF were determined by HPLC.
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