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The first observation of the effect of dendritic structure to produce the triplet excited state of the core stilbene by dendron excitation

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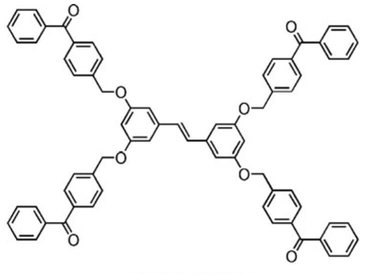
Abstract—We report that both singlet and triplet energy transfers in stilbene-cored benzophenone dendrimers (*trans*-**BPST**) took place quite efficiently. On excitation (290 nm) of stilbene group, the intramolecular singlet energy transfer from the excited core stilbene to the benzophenone part (99.7%) was confirmed by quenching of the fluorescence from the core stilbene. The benzophenone in the excited singlet state is known to undergo intersystem crossing to give its excited triplet state quantitatively. However, the very weak phosphorescence from benzophenone part in *trans*-**BPST** was observed even at 77 K. The phosphorescence intensity of *trans*-**BPST** is only 1% of that of model compound (4-methylbenzophenone) at 77 K. During the irradiation, the absorption spectra also changed due to the trans–cis isomerization. This is probably due to the ultrafast triplet energy transfer from the benzophenone to produce the triplet state stilbene.

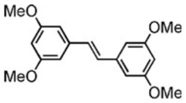
We have been studying the photochemical behavior of stilbene dendrimers having benzylether type dendrons or polyphenylene type dendrons with hydrophobic properties.[1–3] These stilbene dendrimers efficiently underwent trans–cis isomerization even in its fourth generation with the molecular weight as high as 6500. In addition, water soluble dendrimers with benzylether type dendron group bearing hydrophilic carboxylate groups at the periphery have been studied,[4] where one can observe fast and slow structural change, respectively, due to the isomerization around the C=C double bond and the molecular motion of the peripheral dendron group.[5]

The energy transfer in dendrimers has been widely investigated so far.[6] Many of them are related to the singlet energy transfer. Intermolecular triplet energy transfer from the benzophenone core in dendrimers to terbium ion and molecular oxygen[7] and intramolecular triplet energy transfer in dendrimers with the benzophenone at the periphery[8] have also been studied. However, the dendrimer systems where both the intramolecular singlet energy transfer from the core to the periphery and triplet energy transfer from the periphery to the core can be observed in the same molecule have not been reported so far.

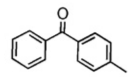
We have reported here a new type of stilbene dendrimers having triplet sensitizer within their molecular structure and studied the energy transfers dynamics and the emission and photoisomerization properties. The aim of this study is to find the features of both triplet and singlet energy transfer as the intramolecular process. In addition, one can expect the ultrafast triplet energy transfer



***trans*-BPST**



***trans*-TMST**



4-MeBP

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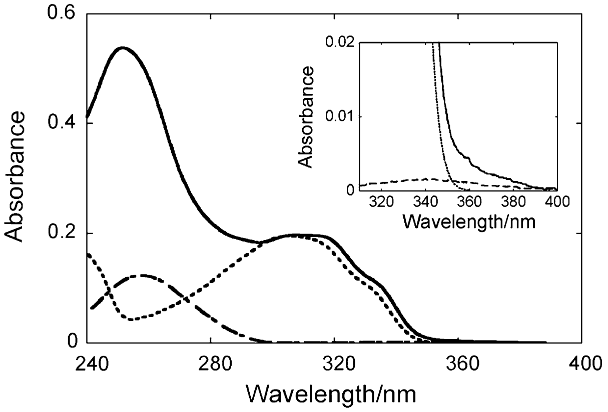

Figure 1. Absorption spectra of *trans*-**BPST** (—, 6.0×10^{-6} M), *trans*-**TMST** (···, 6.0×10^{-6} M) and **4-MeBP** (-–-, 6.0×10^{-6} M) in THF. The inset shows the magnified spectra in the 310–400 nm region.

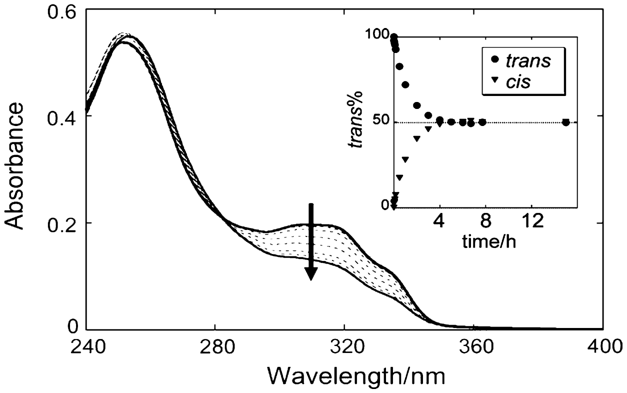

Figure 2. Time dependence of absorption spectra of *trans*-**BPST** (6.0×10^{-6} M) with irradiation at 370 nm (0, 30 s, 1, 10, 30 min, 1, 2, 3, 5, 8, and 15 h) in THF. The inset shows the time dependence of absorbance change observed at 308 nm.

to produce the triplet state stilbene to find the properties and dynamic processes of cis-, trans-, and twisted triplet state.

The *cis*- and *trans*-benzophenone-substituted stilbene dendrimers (**BPST**) were prepared and separated by column chromatography. Their structures were identified by Maldi-Tof-Mass and NMR spectroscopies.

Figure 1 shows the absorption spectra of *trans*-**BPST**, *trans*-tetramethoxystilbene (*trans*-**TMST**), and 4-methylbenzophenone (**4-MeBP**) in THF at room temperature. The absorption band around 300–350 nm with molar extinction coefficient (ε) of $3.2 \times 10^4\,\mathrm{cm^{-1}\,M^{-1}}$ at 308 nm is mainly due to the π–π^* transition of the stilbene unit, while the band at longer wavelength region around 360–390 nm with weak band with ε of $340\,\mathrm{cm^{-1}\,M^{-1}}$ at 370 nm is ascribed to the n–π^* transition of the benzophenone unit. The fluorescence quantum yield of *trans*-**BPST** on excitation at 290 nm was determined to be 0.0008 at room temperature which is only 0.3% of that of *trans*-**TMST** ($\Phi_f = 0.27$).[9] These results suggest that the excited singlet state of stilbene unit (83 kcal/mol)[10] in *trans*-**BPST** is efficiently

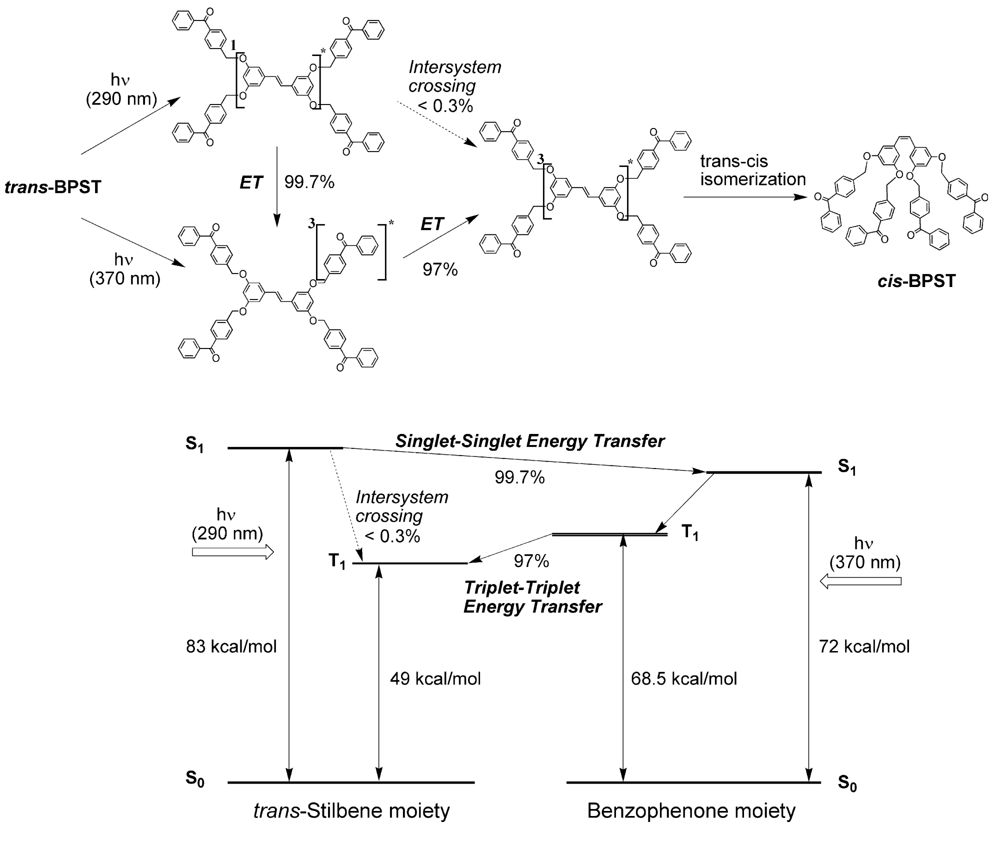

Figure 3. Mechanism of photochemical isomerization and energy diagram for *trans*-**BPST**.

quenched by the surrounding benzophenone group (72 kcal/mol).[11] More precisely it can be said that, in *trans*-**BPST**, efficient energy transfer occurs from the excited singlet state of core stilbene to the peripheral benzophenone unit resulting in the production of the excited singlet state of benzophenone. The efficiency of the singlet energy transfer was estimated to be 99.7%. These results indicate that the efficiency of the intersystem crossing from the excited singlet state of core stilbene to its excited triplet state is less than 0.3%. The phosphorescence spectra of *trans*-**BPST** could not be observed at room temperature, although that for 4-methylbenzophenone (**4-MeBP**) itself was observed. However, the very weak phosphorescence band was observed for *trans*-**BPST** at 77 K. The phosphorescence intensity of *trans*-**BPST** is only 3% of that of **4-MeBP** even at 77 K.

On irradiation at 370 nm light, **BPST** underwent trans–cis isomerization to yield the photostationary state mixture of $[t]/[c] = 50/50$ as revealed by the change of absorption spectra (Fig. 2). The result shows that the excitation of the benzophenone unit on irradiation at 370 nm resulted in only non-radiative decay including trans–cis isomerization. The energy transfer and the isomerization mechanism of **BPST** is summarized in Figure 3. On irradiation at 370 nm, the benzophenone excited singlet state underwent efficient intersystem crossing to give the triplet benzophenone (68.5 kcal/mol),[12] which underwent efficient energy transfer to produce the stilbene triplet state (49 kcal/mol)[12] resulting in the trans–cis isomerization of the core stilbene through the triplet state. The efficiency of energy transfer from benzophenone triplet to *trans*-**BPST** can be estimated to be as high as 97%. The observation that the irradiation at 370 nm light resulted in the trans–cis isomerization indicates that the excitation of benzophenone chromophore only resulted in the intersystem crossing to the triplet state, which in turn gave rise to the stilbene triplet through energy transfer.

In summary, the efficiency of singlet energy transfer from stilbene to benzophenone is estimated to be 99.7% comparing the fluorescence quantum yield of *trans*-**BPST** with that of *trans*-**TMST** on excitation at 290 nm. Furthermore, the energy transfer from the benzophenone triplet to the stilbene is estimated to be 97% as estimated by the phosphorescence spectroscopy. To the best of our knowledge, this is the first clear observation that the dendritic structure can be used to prepare the triplet excited state of the core structure, which is produced by the dendron excitation. The fast kinetic study to observe the triplet energy transfer process in the time scale of less than nanosecond and the isomerization dynamics of stilbene triplet in the time scale of ns is in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.11.109.

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