Feature Article

Synthesis, excited state properties, and dynamic structural change of photoresponsive dendrimers

Atsuya Momotake[a,b], Tatsuo Arai[a,*]

[a]*Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*
[b]*Research Facility Center for Science and Technology, University of Tsukuba, Tsukuba, Ibaraki, Japan*

Abstract

This article reviews recent advances in research of the dendrimer synthesis in connection with the design, synthesis and reaction of photoresponsive dendrimers. Dendrimers with photoreversible stilbene cores undergo mutual *cis–trans* isomerization in organic solvents to give photostationary state mixture of *cis* and *trans* isomers. Even the fourth generation (G4) stilbene dendrimer with molecular weight as high as 6500 underwent *cis–trans* photoisomerization within the lifetime of the excited singlet state. The large dendron group surrounding the photoreactive core may affect the excited state properties of the core to increase the efficiency of photoisomerization and/or decrease the fluorescence efficiency. The photochemistry of stilbene dendrimers with various types of dendron groups, and azobenzene dendrimers is discussed. Furthermore, recent advance of dendrimer syntheses and the possibility of their application to construct photoresponsive large molecules are discussed.
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1. Introduction

Photoisomerization of usual small molecules such as stilbene has been extensively studied and the isomerization mechanism in the excited singlet state as well as in the triplet state has been revealed (Scheme 1) [1–40]. One can classify the photoisomerization mechanisms. One of them is the adiabatic mechanism producing the isomer in the excited state directly in the excited state energy surface (Fig. 1(a)). The other is the diabetic mechanism deactivating from the perpendicular excited state to the ground state producing the isomer along the ground state energy surface from the perpendicular conformation (Fig. 1(b)). From the considerably large number of original reports and the review articles, it seems that the fundamental problems in the isomerization mechanism in the excited state have been clarified. On direct irradiation, the stilbene undergoes mutual isomerization between the *cis* and *trans* isomers, deactivating from the perpendicular conformation of the excited singlet state (Scheme 1, Fig. 2). The singlet excited

state of *trans*-stilbene does not undergo the intersystem crossing to the triplet excited state at room temperature in fluid solution. The *trans* isomer in the excited singlet state undergoes isomerization to the *cis* isomer with a quantum yield of ∼0.5 or gives fluorescence emission with a quantum yield of 0.04, decaying by 70 ps [14,23]. The *cis* isomer in the singlet excited state produces practically no fluorescence and undergoes either *cis*-to-*trans* isomerization or cyclization to form dihydrophenanthrene (DHP) [17]. The oxidation of dihydrophenanthrene gave phenanthrene, which is used to prepare substituent phenanthrene from appropriate precursors. Under nitrogen atmosphere without any oxidant, dihydrophenanthrene usually reverts to the starting *cis* isomer. Since the mechanism so-called non-vertical excitation transfer from the sensitizer to the *cis*-stilbene was proposed at the early stage of the mechanistic photochemistry of stilbene, its role and the possibility of adiabatic *cis*-to-*trans* isomerization in the excited state are still under discussion [23].

Despite widespread investigation for stilbenes, there are still some areas of controversy. One of them is the stilbene photochemistry in viscous media or in microheterogeneous media such as micells, vesicles or Langmuir–Blodgett (LB)

* Corresponding author. Tel./fax: +81-298-53-4315.
  E-mail address: arai@chem.tsukuba.ac.jp (T. Arai).
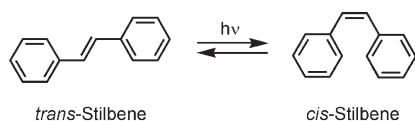
Scheme 1.

films, since stilbene photochemistry is strongly dependent on viscosity and temperature [41,42].

Whitten et al. developed stilbene surfactant probes for hydrophobic sites in micelles, vesicles, and other assemblies (Fig. 3) [43–45]. Although the use of probes, whose properties in the medium can be monitored by various spectroscopic techniques, gave useful information [46–49], there are the possibilities for the specific properties of many probes to create a special microenvironment, and the obtained results may be different probe dependent. Among them, the stilbene chromophore appeared to be an attractive probe. Stilbene is a more or less liner hydrocarbon, which should be hydrophobic. In addition, stilbenes readily functionalized with fatty acids to make surfactant molecules with stilbene probes. The synthesized stilbene surfactants actually exhibited the different photochemical properties in different media. For example, the photochemical behaviors of stilbene surfactants were studied with methyl viologen (MV^{2+}) in SDS micelles [50,51] to investigate solute partitioning in aqueous surfactant assemblies, in supported multilayer and films at the air–water interface [52], or in homogenious (benzene and methylcyclohexane) solutions [53].

One of the other uncertain areas for stilbene photochemistry is the effect of the highly organized or congested media on the photochemical behaviors of stilbene. There are several interesting photochemical events in biologically important chromoproteins such as rhodopsin and phytochrome, where the chemical molecules are covalently bounded to the surrounding proteins (Scheme 2) [54–66]. Although it can be easily understood that the photon triggers the isomerization of the chemical chromophores in these biomolecules, it seems rather difficult to understand the really occurring dynamic mechanisms in the isomerization of chemical chromophore in these large biomolecules. By the approach from the chemistry, R.S.H. Liu proposed an interesting isomerization mechanism around the C=C double bond in biomolecules [67–71]: the isomerization
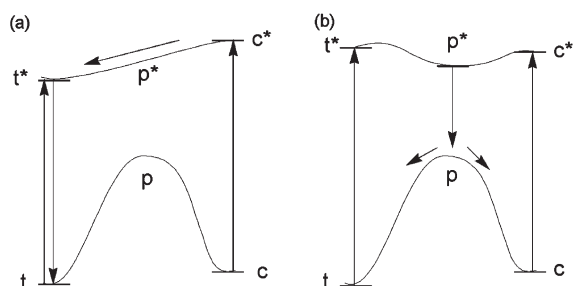

Fig. 1. Potential energy surfaces of isomerization in the adiabatic mechanism (a) and the diabatic mechanism (b).
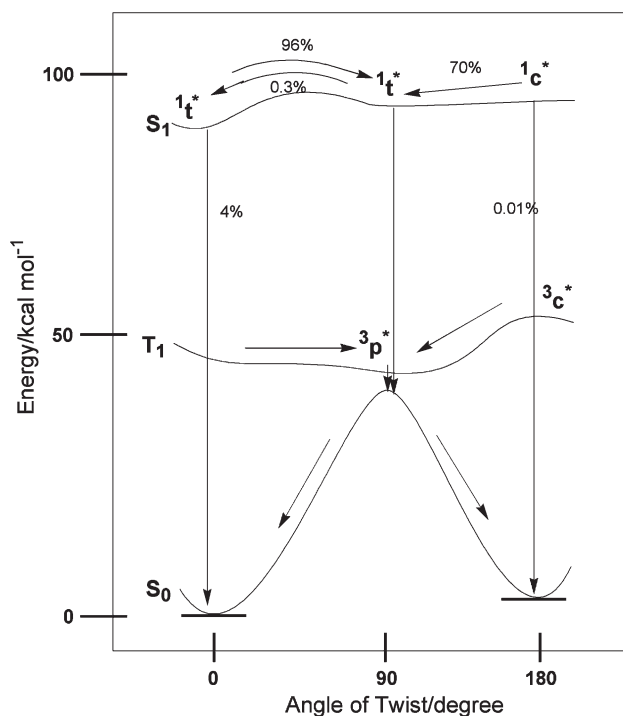

Fig. 2. Potential energy surfaces of isomerization of stilbene in the excited singlet and triplet state [22].

in largely congested environment should proceed not by a simple 180 degree rotation of the C=C double bond but by the concomitant twisting of the single bond and the double bond (Scheme 3). There should be other important mechanism in the structural changes of large molecules in the excited state. From these points of view, it is worth studying the photochemical structural changes of dendrimer molecules having photoresponsive chromophore. The dendrimer has a unimolecular weight with well defined structure but has some flexibility of the three dimensional way. Furthermore, the fundamental approach to find a novel mechanism on structural change of large molecules triggered by the ultra fast geometrical isomerization of one of the part of the large molecules should be quite important as a basic study to construct a novel photofunctionalized molecule for application purposes.

We wish to review here the recent dendrimer synthesis and photochemistry of photoresponsive dendrimers. First, the recent divergent and convergent approaches for the dendrimer construction in relation to the design of photoresponsive dendrimers will be mentioned. Second, the photochemical behavior of stilbene dendrimers having either benzyl ether-type dendrons or polyphenylene-type dendrons in organic solvents will be described [108–110,
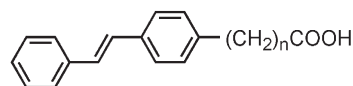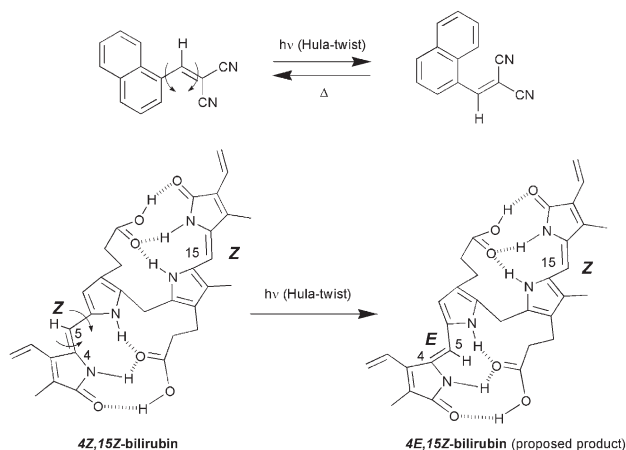

Surfactant stilbene

Fig. 3. Structure of surfactant stilbene.
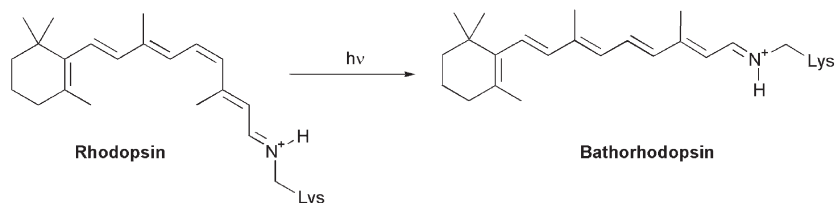
Scheme 2. Primary photoproduct from rhodopsin and the all-*trans*-6-*cis* structure of bathorhodopsin [69].

115–118] and the introduction of hydrophilic substituents at the periphery of benzyl ether-type dendrimers will be mentioned [111,114]. Then, other photoresponsive dendrimers such as azobenzene dendrimers will be briefly introduced [119–135].

At this stage, we should briefly mention here the feature of dendrimers. Dendrimers are highly branched monodisperse molecules in the nanometer scale. There are three parts of location for the functional groups to be placed, i.e. the core, surface groups, and branching units of dendrimers (Fig. 4) [72]. The molecular shape of the dendrimers largely depends on their generations. Due to steric effects, increasing the generation of dendrimer leads to a sphere shaped molecule until steric overcrowding avoids complete reaction. This steric limitation leads to small molecular sizes, but high molecular weights can be obtained due to the high density of the end groups at the periphery. There are two distinct chemical environments in dendrimers: the surface chemistry, coming from the functional groups at the periphery in dendrimer, represents the molecular features such as solubility, and the interior, shielded from outside environments due to the high density at periphery and spherical molecular shape of the dendrimers. The difference between the outside environment and the sphere's interior may be emphasized by using water-soluble dendrimer (WSD) with hydrophobic interior. These two different environments may play an important role in host–guest or caging–uncaging chemistry. In this context, a combination of dendrimers and photoresponsive molecules is quite attractive.

2. Dendrimer synthesis

Dendrimer synthesis is one of the new fields of polymer chemistry. Unlike chain reaction for polymer synthesis, synthesizing dendrimers demands stepwise reactions, which build the dendrimer up one generation (or one monomer layer) at a time. Each dendrimer consists of a multifunctional core molecule with a dendritic wedge attached to each functional site. The core molecule without surrounding dendrons is usually referred to as zeros generation. Each successive repeat unit along all branches forms the next generation, 1st generation and 2nd generation and so on until the terminating generation. The synthetic methods of both divergent and convergent approaches have been developed by many researchers. We wish to introduce here the recent development of the dendrimer synthesis with their structures. In addition, we will also show some possibilities of the preparation of photoresponsive dendrimers using these dendrimers.

2.1. Divergent methods and photoresponsive dendrimers

The idea of the dendrimer synthesis is simple. Two defined approaches, the divergent synthesis and the convergent synthesis, or both of them, have been used for the almost all dendrimers. In the divergent method, the molecule is assembled from the core to the periphery (Scheme 4). The divergent synthesis is initiated by the

Scheme 3. Photoisomerization of naphthyl analogue [70] and bilirubin by Hula–Twist mechanism [67].
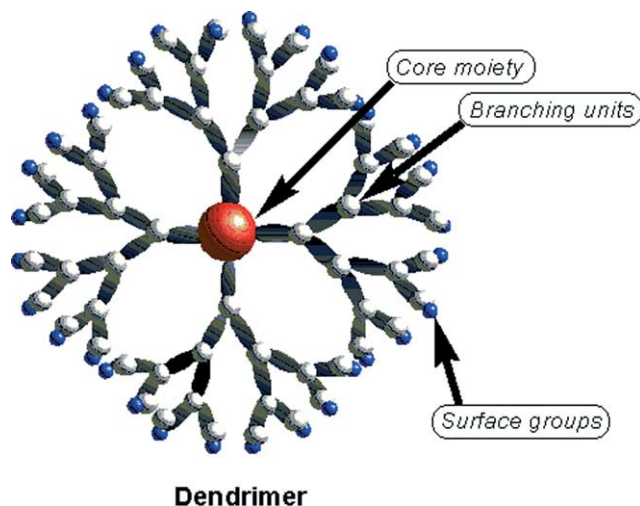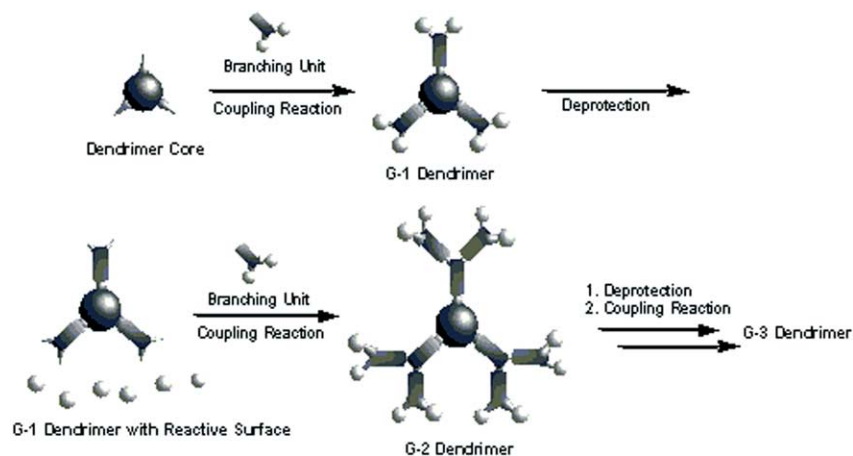
Fig. 4. Constitutional units of dendrimer: core, branching units and surface groups.

Scheme 4.

coupling reaction of the core and a dendron monomer, which usually has one reactive group for coupling with core, and more than one deactivated group at the out side to prevent random polymerization. Thus, the obtained first generation dendrimer has deactivated functional groups at their surface, which are converted to reactive species by deprotection or changing functional groups for the next stage reaction. In this approach, the number of reactive groups at the periphery doubles whenever a generation increases if the dendritic wedge branches to two ways. It is characteristic for divergent methods and may cause difficulties. A potential problem, which may cause as the increase generations, is the difficulties of the purification of the higher generation dendrimer, which is caused by the incomplete reactions of the terminal groups. However, there are some recent divergent approaches, which have conquered these problems by using appropriate reagents or well-selected monomer building blocks. Furthermore, the divergent method has an advantage of being able to yield higher generation dendrimers rapidly and extensively.

When the divergent approaches are used for the photoresponsive dendrimer synthesis, the additional potential problems would be arisen; especially the photoresponsive molecules are used as dendrimer core. That is; the photosensitive core moiety will have a chance to be exposed to room light throughout the synthesis because the divergent method is started with a core molecule. It is real and substantive problem because once the photoresponsive moiety reacts to give another isomer or photoproducts, all dendrimers prepared will be seriously damaged. On the other hand, the photoresponsive molecules are used as the end groups, this undesirable opportunity will be reduced (Fig. 5). In this case, the reaction of dendrimer with photoresponsive molecules should proceed efficiently and completely because of the difficulty of purification. There are some representative examples of the photoresponsive molecules which can be used for photoresponsive dendrimers: (1) photoisomerizable molecules like stilbenes or azobenzenes, (2) phototautomerizable chalcones and qui-

nolines, exhibiting excited-state intramolecular proton transfer, and (3) the combination of the photo-induced electron donor–acceptor molecules.

As one example of photoresponsive dendrimers, using poly(propyleneimine) dendrimers prepared by divergent method, Vögtle et al. reported the azobenzene dendrimers having up to 32 azobenzenes in the periphery (Scheme 5) [73]. These dendrimers were used as potential hosts for eosin Y. Both the E and Z forms of the azobenzene groups at the periphery of the dendrimers quench the eosin fluorescence by amine units in the branches of the dendrimers. The fluorescence experiment showed that eosin is hosted in the dendrimers and suggested that the Z-isomer of the dendrimers were better hosts than the E-forms.

Meijer et al. developed another example of photoresponsive poly(propylene imine) dendrimers, functionalized with oligo(p-phenylenevinylene)s (OPVs) in the periphery [74]. This OPV dendrimers self-assembled at the air–water interface forming homogeneous thin films. The OPV dendrimers extract dyes efficiently from aqueous solution into non-polar solvents. The thin films composed of OPV dendrimers and dyes exhibited efficient energy transfer. Thus, dendrimers, obtained by divergent method, seem to be suitable for the development of photoresponsive dendrimers with photoresponsive units at their surface.

2.2. Recent divergent methods

With the divergent/divergent approach, Twyman et al. synthesized unsymmetrical dendrimers, possessing methyl ester groups on one surface, and iso-butylamide groups on the opposite surface (Scheme 6) [75]. The synthesis started with the alkylation of BOC protected ethylene diamine with methyl acrylate followed by amidation with excess ethylene diamine, which is standard PAMAM dendrimer method [76]. The growth of the first half of the unsymmetrical dendrimer terminated by the addition of iso-butyl amine and then BOC-protecting group at the core was removed to give free amino group for development of the opposite side
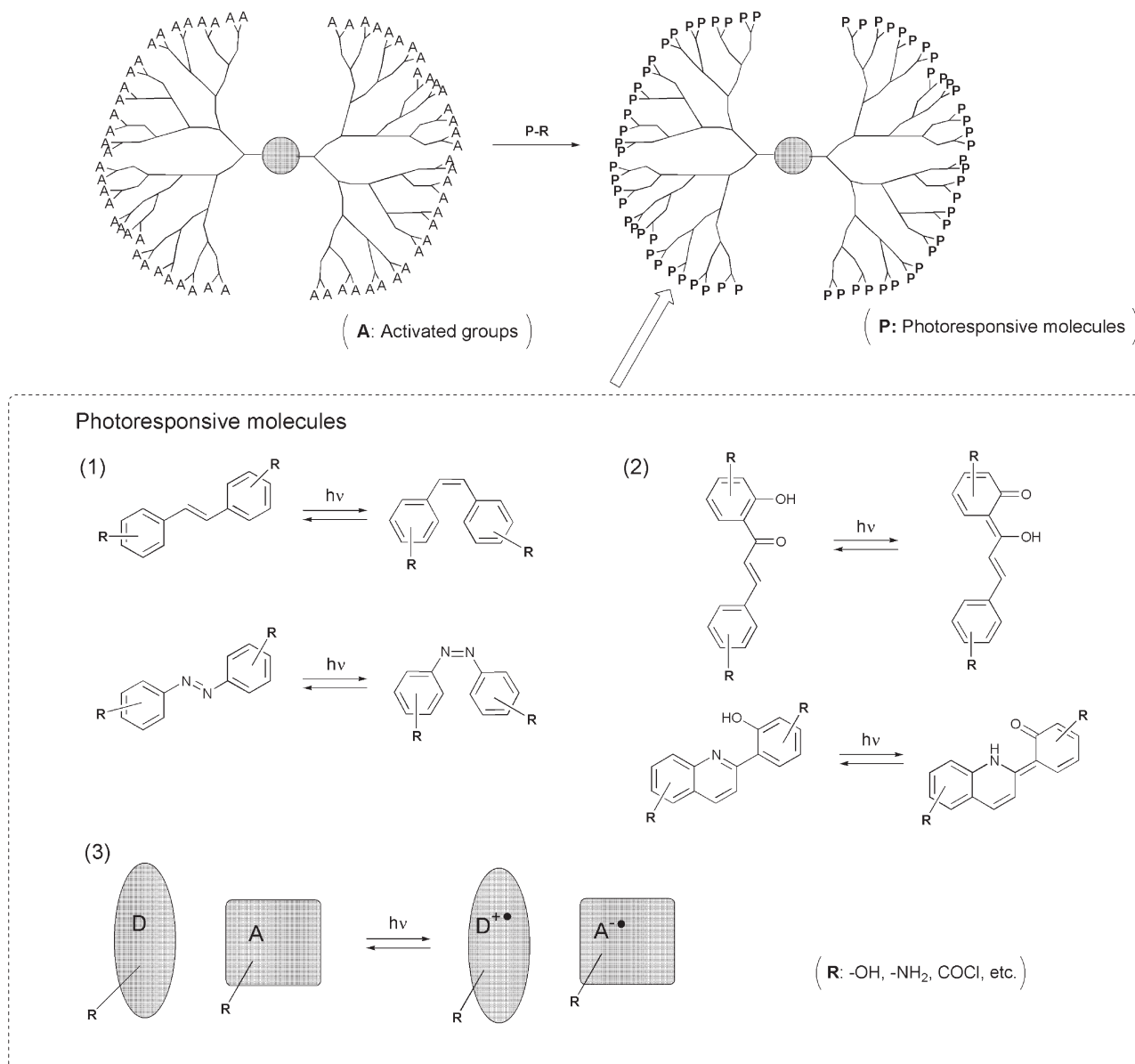
Fig. 5. Synthetic approach to dendrimers with photoresponsive molecules on the surface.

dendron. All unsymmetrical PAMAM dendrimers were obtained in excellent yields without or with little purification. With this approach, it would be possible to prepare the unsymmetrical photoresponsive dendrimers with two different photoresponsive units at different peripheries.

Fréchet and coworkers developed a new divergent approach for the synthesis of aliphatic polyester based dendrimers (Scheme 7) [77]. The key of this method is to prepare the benzylidene-protected anhydride building block, which is used as the efficient acylating agent. Unlike the other usual divergent synthesis, the coupling reaction of the building block and the phenolic core molecule took place using only little excess of anhydride (1.25 equiv.) against the core to afford very good yield. Both the esterification reaction and the subsequent deprotection reaction of the benzylidene groups by hydrogenolysis

using Pd–C are clean and the products are essentially pure after simple purification. A monodispersed G6 polyester tridendron dendrimer with a molecular weight of 30,711 Da as well as other series of dendrimers were obtained.

For the same divergent approach, poly(p-hydroxystyrene) (PHS) was chosen as low polydispersity liner backbone [78]. The average molecular weight of PHS polymer samples used are 4450 and 10,200. Use of the high polar solvents like DMF suppress, the side reaction and DMF/Pyridine mixed solvent afforded the G4 dendrimer for shorter PHS backbone and the G3 for the longer PHS backbone. The results showed the efficiency and the flexibility of this divergent approach.

Isopropylidene was also used as a protecting group for anhydride building block which is the key molecules for this
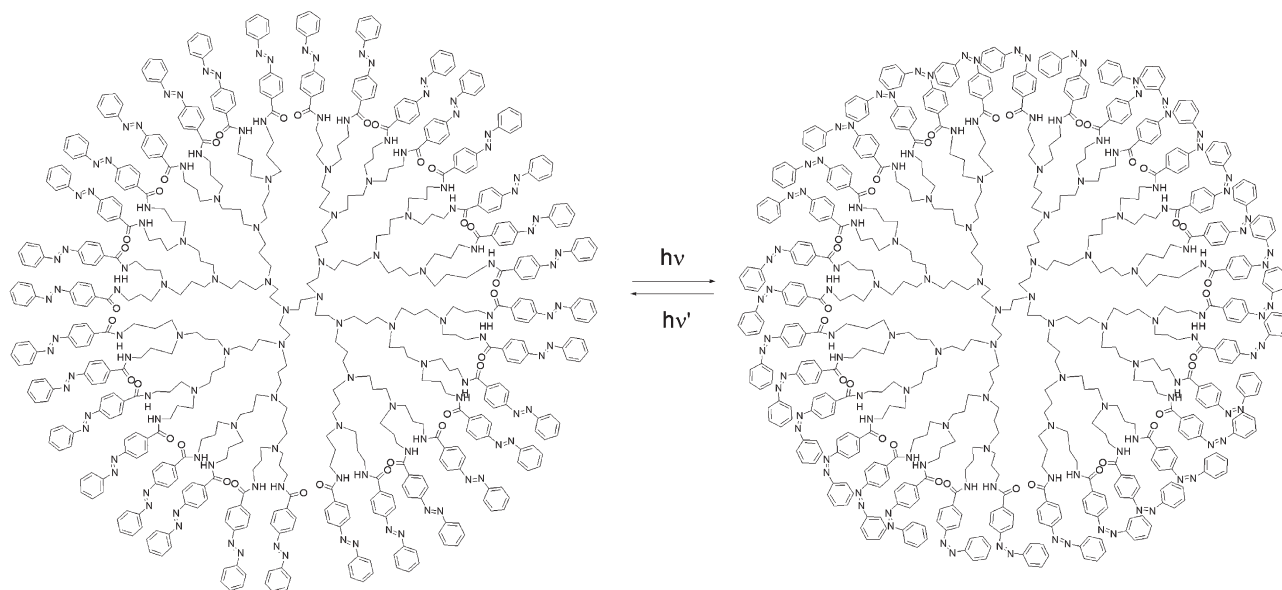
Scheme 5. Photoisomerization of azobenzenes in G4 dendrimer. *E*-form (left) and *Z*-form (right).
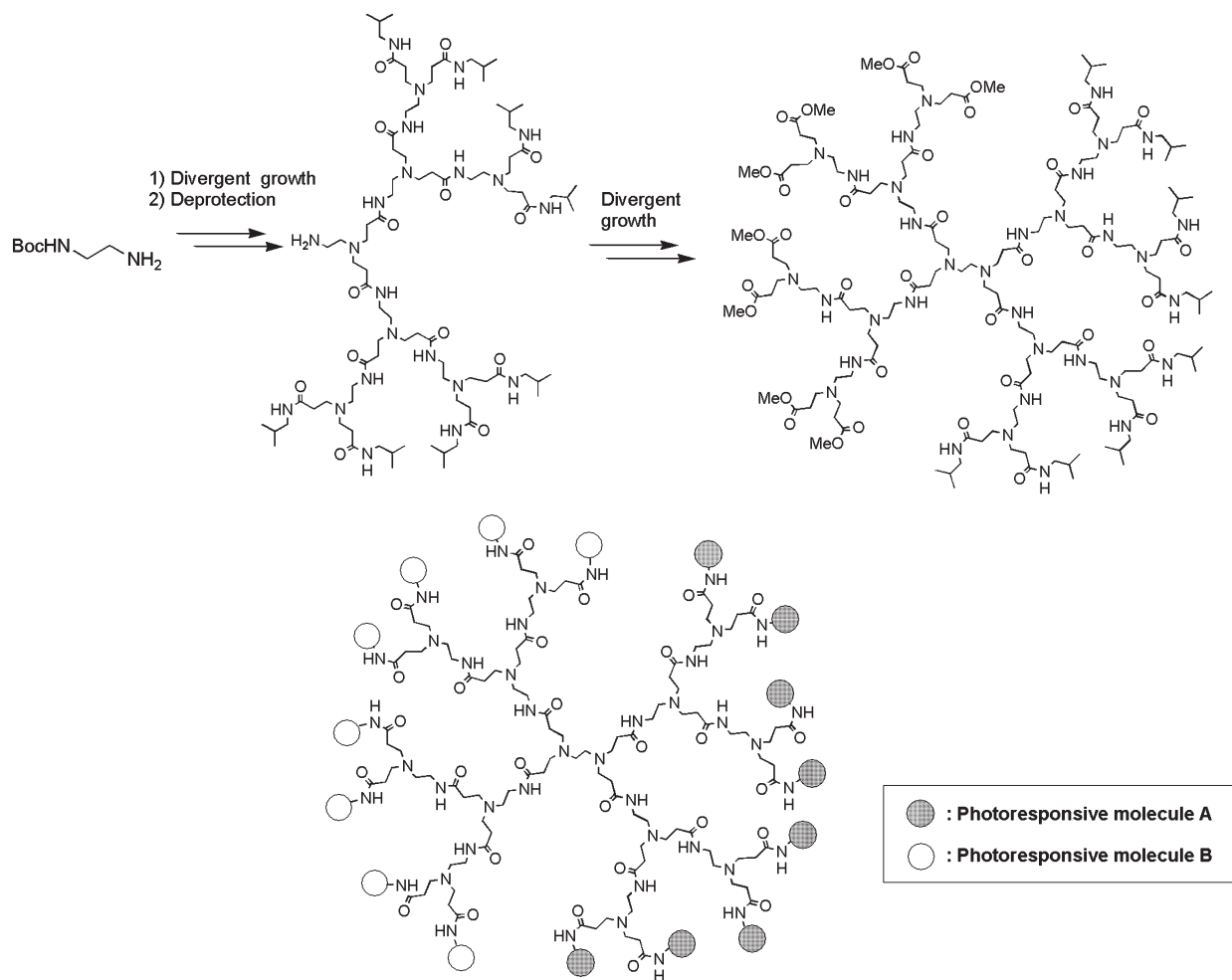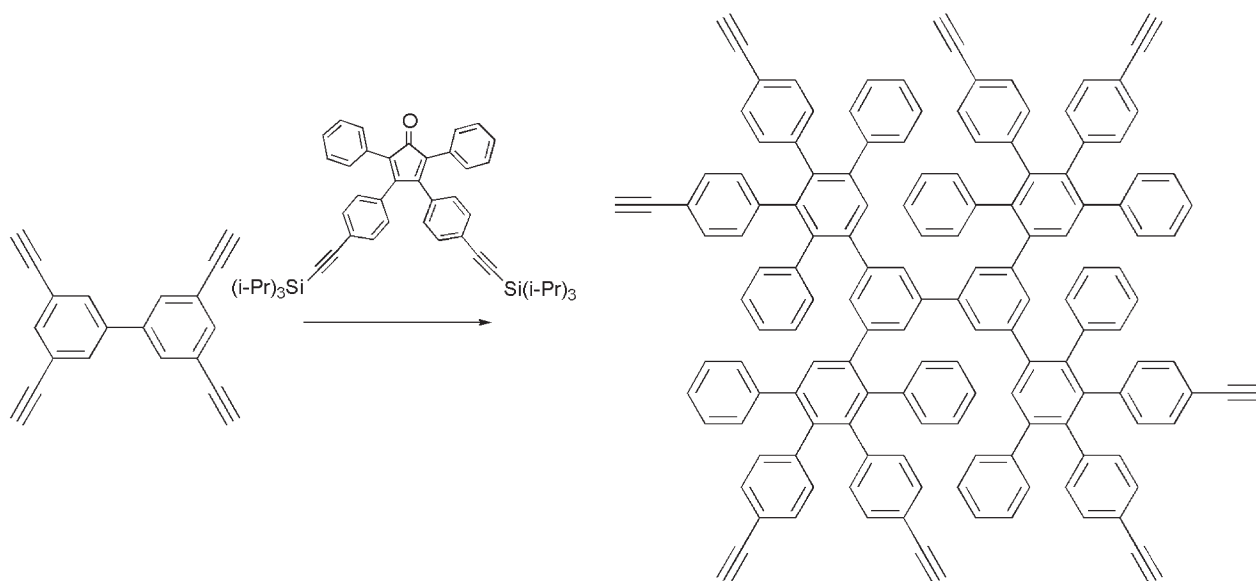

Scheme 6.
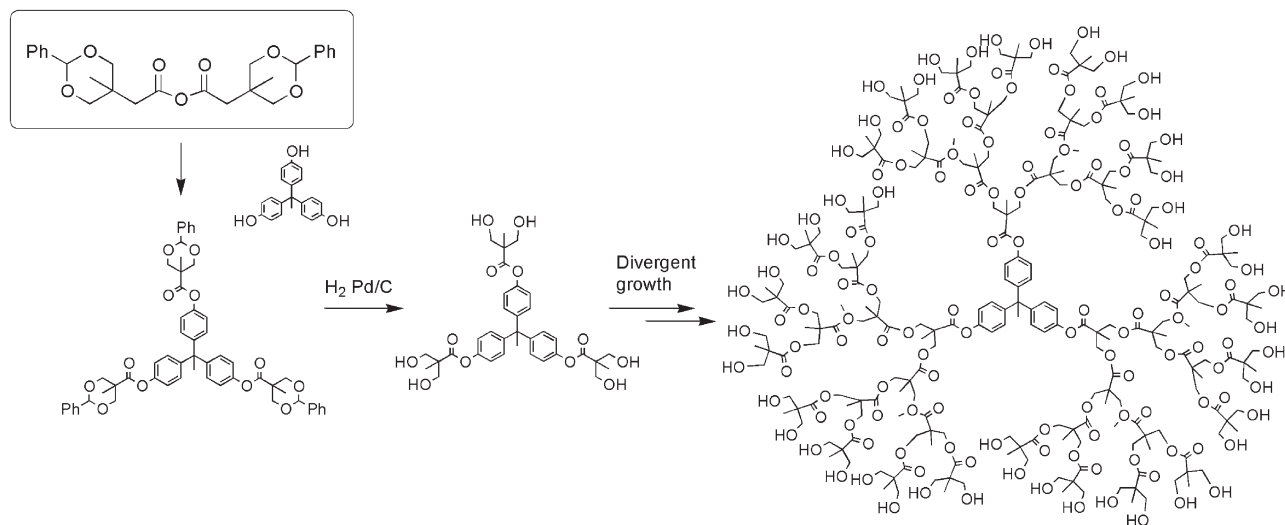
Scheme 7.

divergent approach [79]. The methodology is similar to that in Fréchet's report and the procedure was employed to the synthesis of G4 dendron in 65% overall yield.

With the [2 + 4] Diels–Alder cycloaddition of a tetraphenylcyclopentadienone to an ethynyl compound, Müllen et al synthesized monodisperse polyphenylene dendrimer up to G4 using divergent approach (Scheme 8) [80]. The shape of the obtained dendrimers, dumbbell-, tetrahedral-, and propeller like structure, were controlled by using the biphenylene, tetraefric, trigonal, and hexagonal cores which allows the dendrimer branches growing the different direction and density. These stiff dendrimers of G3 and G4 were visualized by TEM. Hereinafter, only the recent divergent syntheses will be described.

Generally, the dendrimer synthesis in divergent approach requires two steps: coupling reaction and deprotection/activation reaction, plus following purification for each step. To reduce the number of reaction steps for growing the dendrimers, the dendrimer synthesis such as double stage method have been developed. Among these, one of the easiest ways to grow the dendrimer is reported by Caminade and Majoral groups [81]. In this synthesis of phosphorus-containing dendrimer, neither deprotection steps nor purification is needed since the designed two types of AB_2 monomer units do not have any protecting groups. The each growing reaction proceeds quantitatively (Scheme 9). Furthermore, this sequence of growing reaction does not need any isolation because the by-products are only N_2 and H_2O. Thus the one-pot experiment for the synthesis of dendrimer was demonstrated and the obtained G4 dendrimer was rather clean.

As a very recent application of this methodology, the phosphorus dendrimers up to G5 having a hydrophobic interior and hydrophilic groups (ammonium salts) at the
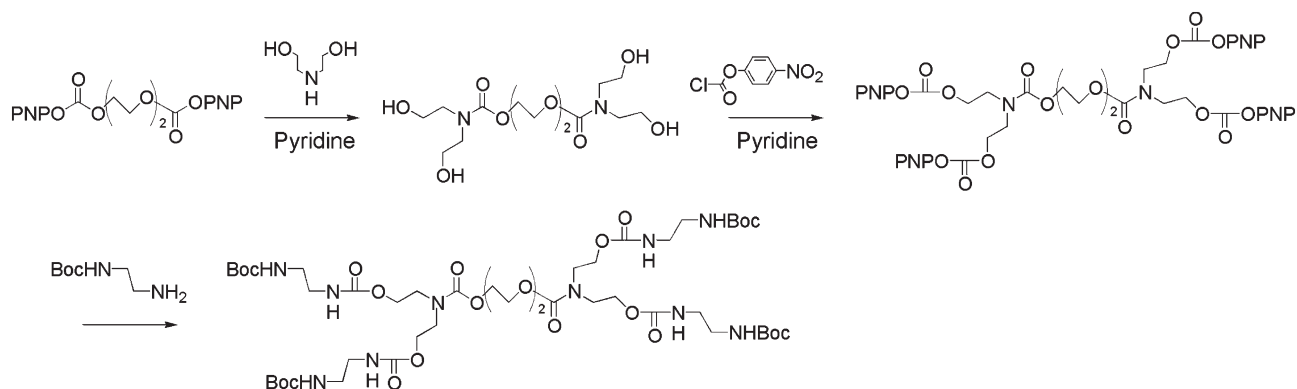

Scheme 8.
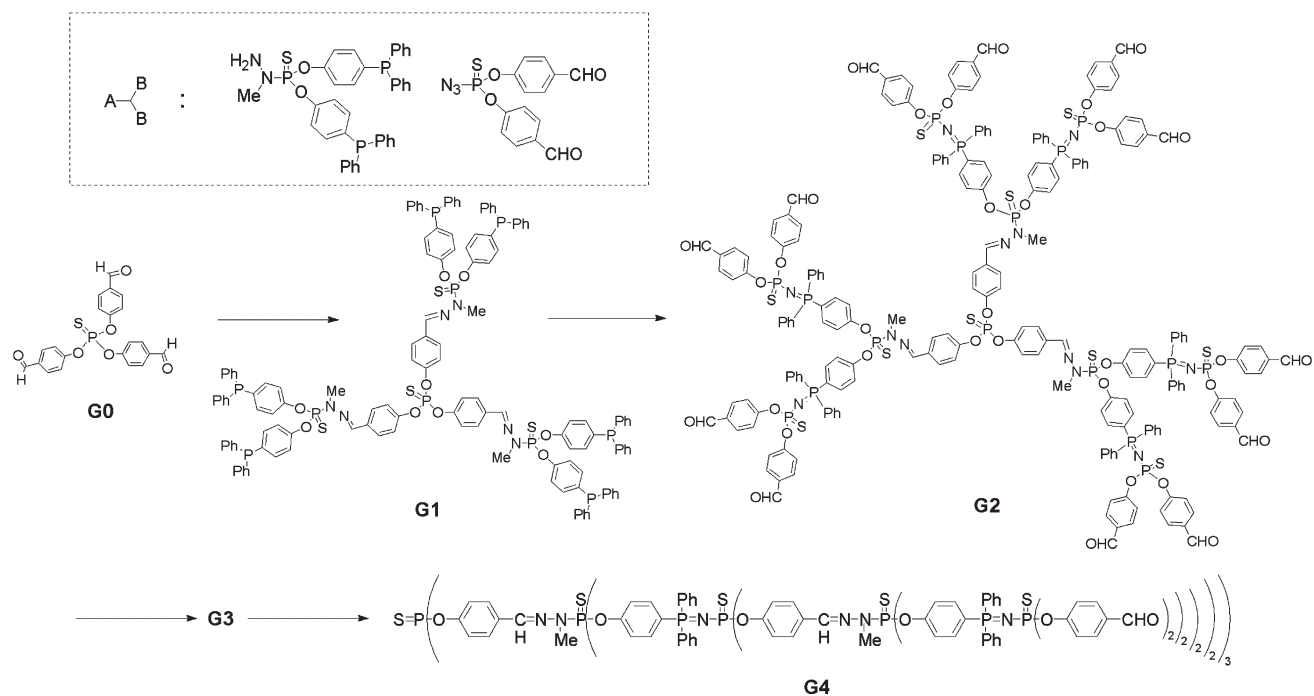
Scheme 9.

periphery were synthesized as nanomeric sponges, which were studied using the pulsed-fields gradient spin-echo NMR technique in water [82].

Carbamates are attractive compounds in terms of biocompatibility because of being more metabolically stable than esters, more resistant to proteases than amides and lack of toxicity and immunogenicity. However, carbamates have seldom been used for dendrimer backbone. For new divergent approach, Ton-Nu et al. used relatively less activated carbonate derivatives, 4-nitrophenyl (PNP)-carbonate esters, which are reactive to acylate amines but not reactive with hydroxyl groups (Scheme 10) [83]. The synthesis is initiated by treating core alcohol with PNP-chloroformate. Then PNP carbonate reacts with diethanol amine, branching units, to give next generation of dendrimer. The peripheral hydroxyl groups can by converted in situ to PNP-carbonate esters again.

When *tert*-amino groups are used as branching units in

dendrimer, acrylates are one of good candidates for their precursors. In this divergent approach, the synthesis was started with the coupling reaction of piperazine with acryloyl chloride (Scheme 11) [84]. Following Michel reaction between diethanolamine and the acrylate periphery was accomplished using only 1.05 equiv. of diethanolamine to give $G1(OH)_4$. Then, $G1(OH)_4$ was treated with acryloyl chloride followed by Michael reaction again to produce $G2(OH)_8$. Thus, the used monomeric building blocks in this method are only readily available diethanolamine and acryloyl chloride. $G3(acrylate)_{16}$ bearing 16 acrylate groups at the periphery was obtained.

Organometallic dendrimers have been focused on much attention due to their interesting optical, electronic and magnetic properties [85–88]. The majority of organometallic dendrimers contain metallic species located at the periphery or at the core. Therefore, the syntheses of dendrimers containing organometallic complex at the
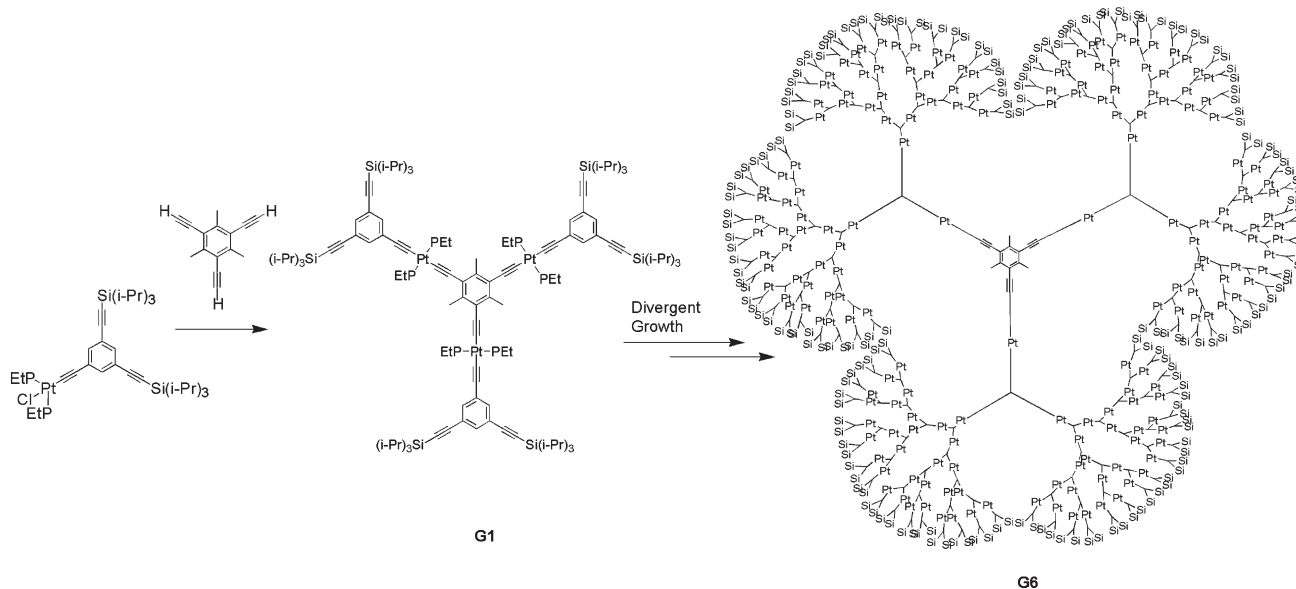

Scheme 10.
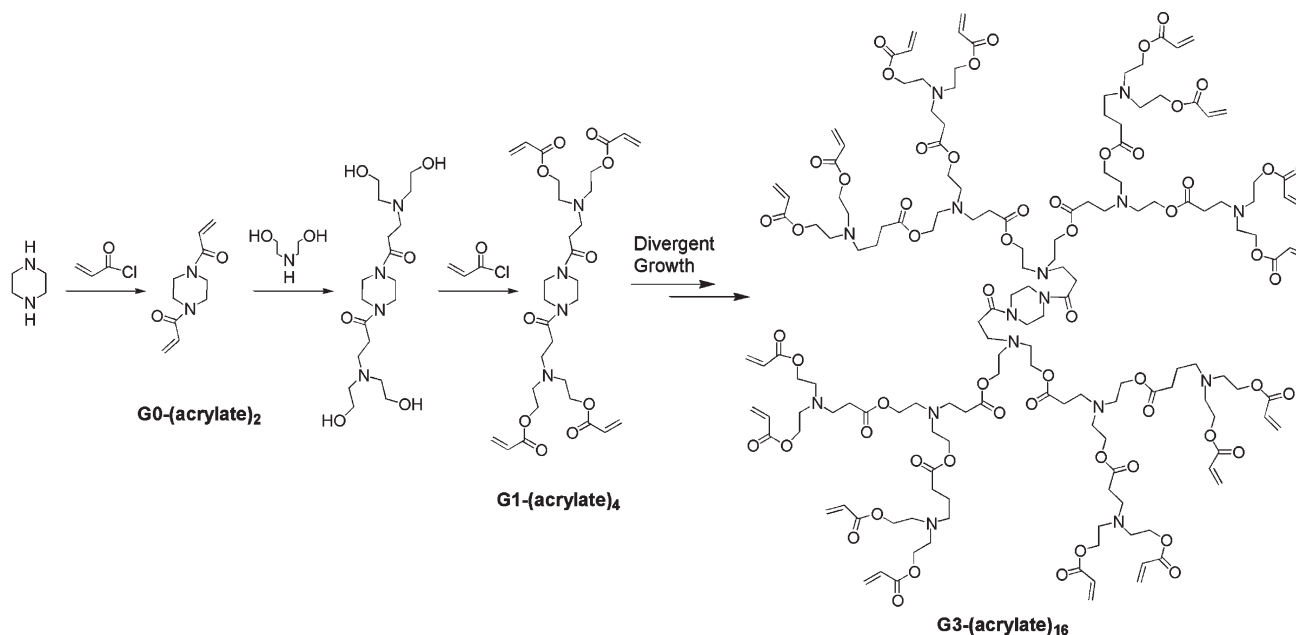
Scheme 11.

branching unit in each generation are still challenge. As shown in Scheme 12, Takahashi et al. synthesized huge platinum-acetylide dendrimers by divergent approach [89]. Platinum–acetylide complexes are thermally stable under air or even moisture and the synthetic methodology is well established. The sixth generation dendrimer containing 189 Pt atoms with the diameter of larger than 10 nm was precisely synthesized.

When each dendrimer monomeric building blocks are connected by ester linkage, further reaction is strongly limited due to their reactivity. Thus, Gitsov et al. chose the divergent strategy with appropriate protecting groups as well as coupling conditions for the poly(ethylene glycol) (PEG)-based poly(benzyl ester) dendrimer synthesis [90]. G1 and G2 dendrimers were obtained in high yields with chemical purity. In addition, G2 dendimers having benzyl or benzoyl protecting groups at the surface self-assemble in water at very low concentration, whereas non-protected G2 dendrimer, having OH end groups, exhibited complete water-solubility at the same concentration.

Giant organo-silicone-based dendrimers using triallyl-phenol building block have been synthesized by divergent method up to ninth generation (Scheme 13) [91]. At ninth generation, the theoretical number of the end groups at the periphery is 177,147 and at least more than 10^5 terminal

Scheme 12.
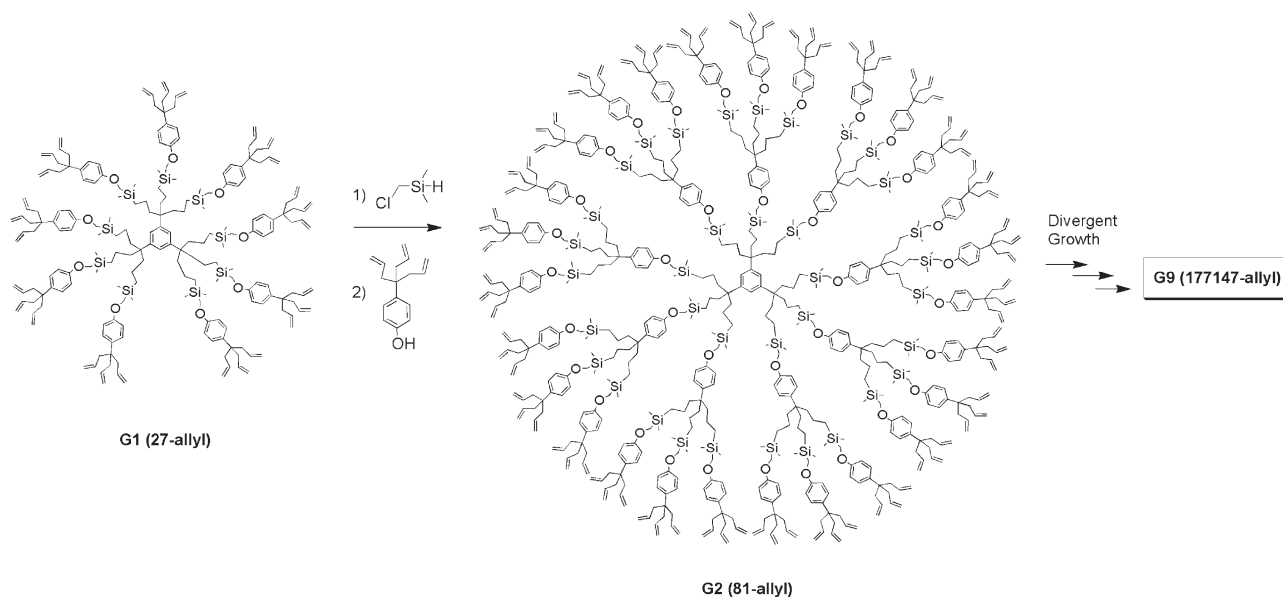
Scheme 13.

groups are actually present in the G9 dendrimer, which is far beyond the dense-packing limit (6000 branches) [92]. It is believed that the flexible branch termini turn inside toward the dendrimer core. From the results, Ruiz et al. proposed that the dendrimer construction probably limited by the density inside the dendrimer rather than by the bulk of the terminal groups at the periphery.

Poly(aryl benzyl ether) dendrons, inverse of Fréchet-type

dendrons, were synthesized by divergent method on Wang resin (Scheme 14) [93]. Dendrimers were prepared to the third generation by Mitsunobu reaction and ester reduction iterative sequence with selected reagents: triphenylphosphine–sulfonamide betaine for Mitsunobu reaction and LiBH$_4$ for ester reduction, respectively. The overall yield of resin G3 is 82%. The dendronized resins were remarkably affected of their swelling behavior.
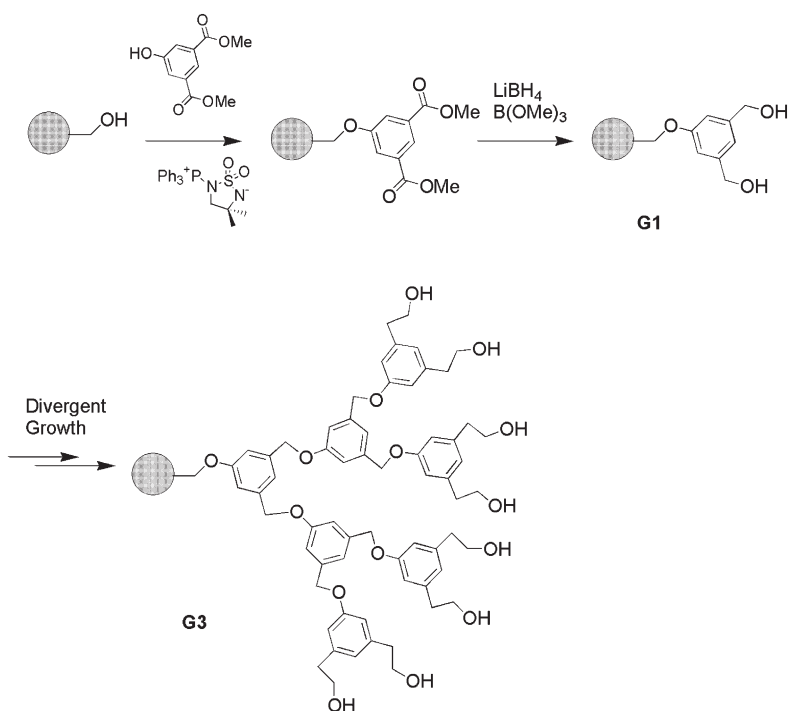
Scheme 14.

3. Design of photoresponsive dendrimers using convergent approaches

3.1. Recent convergent method

In the convergent method, the opposite approach, developed by Hawker and Fréchet [94], the dendrimer is synthesized starting at the periphery and terminating at the core (Scheme 15). The reactive species in the convergent approach must be on the focal point of the dendritic wedge, which makes the reacting point to keep constant. In addition, the small number of reacting points per molecule limits secondary or incomplete reactions, which makes easier their purification and characterization. However, this method does not always allow to built high generations of dendrimers because increase the generation strongly affects the reactivity of focal point due to the steric hindrance. The number of possible generations can be increased by using longer spacing units in the branches of the core molecule.

Convergent synthesis and its application have been already reviewed by Grayson and Fréchet in 2001 [95]. Therefore, we briefly introduce here some very recent reports for the convergent method.

As mentioned above, the syntheses of dendrimers containing organometallic complex at the branching unit in each generation are a current challenge. Humphrey and coworkers developed a facile convergent synthesis of Ruthenium-containing π-delocalized organometallic dendrimers [96]. Ru-containing dendrimers and dendrons were prepared and were characterized by UV, IR, ^{31}P NMR, Mass and TEM.

Rapid convergent synthesis of polyamide dendrimers using unprotected AB_2 monomer building block were

reported by Ueda et at (Scheme 16) [97]. The key of this method is to use of the AB_2 building block containing one carboxylic acid and two amino groups, which react with the end carboxyl group activated by diphenyl (2,3-dihydro-2-thioxo-3-banzoxazoyl)phosphonate (DBOP). Thus, this convergent method requires only two steps for glowing dendrimer: (1) the activation of carboxylic acid by DBOP and (2) condensation reaction of the activated acid with amine. Furthermore, each glowing steps proceeds high yields and simple solvent extraction and reprecipitation are needed for purification.

However, DBOP is an expensive reagent especially for large scale synthesis. Therefore, $SOCl_2$ was used as an inexpensive, common condensing reagent for the same dendrimer synthesis [98]. In this method, each dendron was purified simply by reprecipitation and the reaction yields are 98, 92 and 72% for G1, G2 and G3, respectively. This methodology is more suitable for large-scale convergent dendrimer synthesis than that with DBOP.

The high-yield convergent method for poly(glycerol-succinic acid)-based dendrimers was reported by Grinstaff and coworkers (Scheme 17) [99]. Use of the two selected protecting groups, benzylidene acetal for the protection of 1,3-dihydroxy groups of peripheral glycerol and TBDPS ester for protection of the carboxylic acid of succinic acid, were the key of this method. Since the benzylidene acetal group and TBDPS group can be selectively removed, both convergent and divergent approaches can be used to glow the dendrons in this method.

Syntheses of aliphatic polyurethane homodendrimers were described by Rannard and cowokers (Scheme 18) [100]. Carbonyl containing imidazole compound, which selectively reacts with primary amines [101], was used for
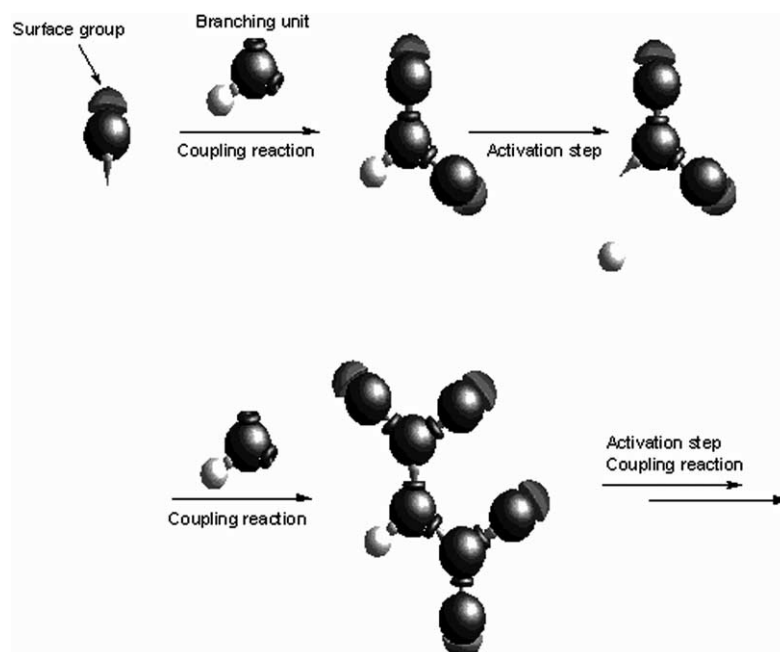
Scheme 15.
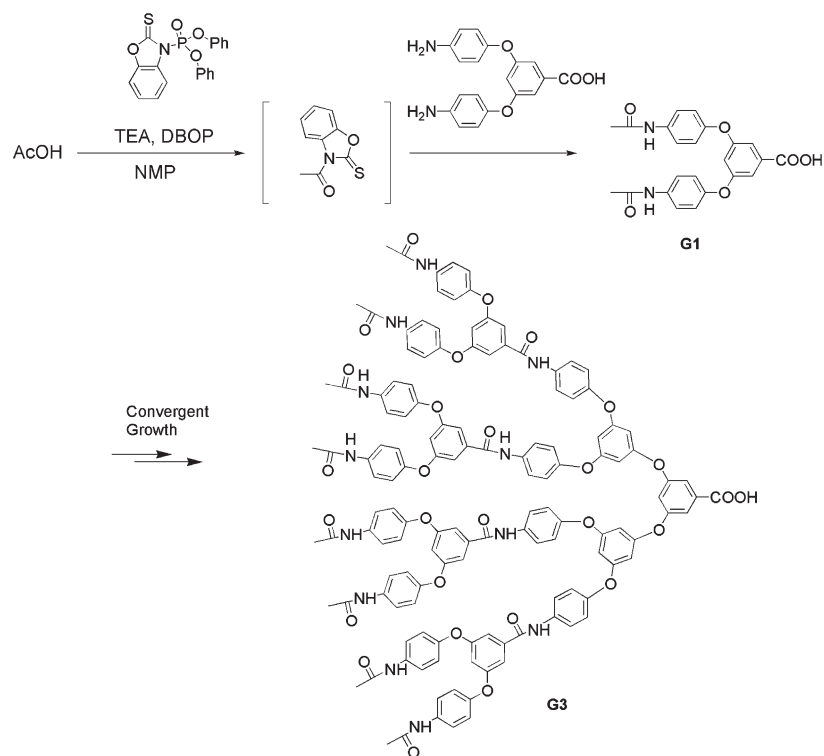
Scheme 16.

urethane linkages. Up to fourth generation of dendrons, with Boc-protected amino surface, were synthesized.

3.2. Design of photoresponsive molecule-cored dendrimers

Design of photo-functionalized molecules is important issue in the view point of photo-energy transduction to chemical energy. Due to their well defined tree-like structure, dendrimers have been attracted increasing attention as artificial light-harvesting systems [102,103].

The light harvesting process takes place by transport of energy absorbed at the end groups (or at the branching units), through the branching units to the core moiety. In this case, the core moiety should be functionalized with an appropriate dye, as an energy acceptor then the acceptor may be able to trigger the subsequent events. In addition, the whole dendrimer structure must show photostability as well, except the case in which the photo-decomposition of dendrimer is an aim [104]. Furthermore, not only physical-, but also chemical- and biological-stabilities would be required for use of the
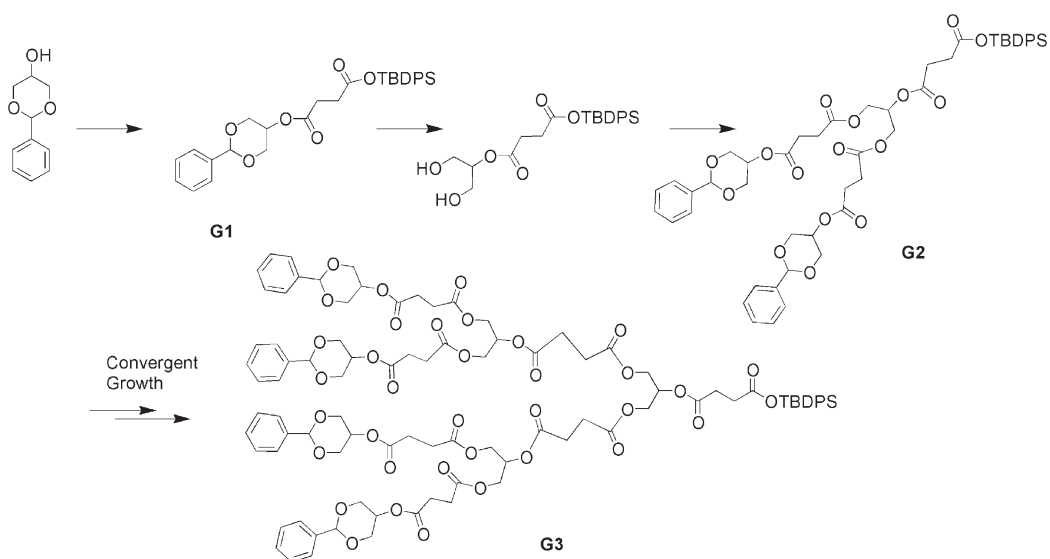
Scheme 17.
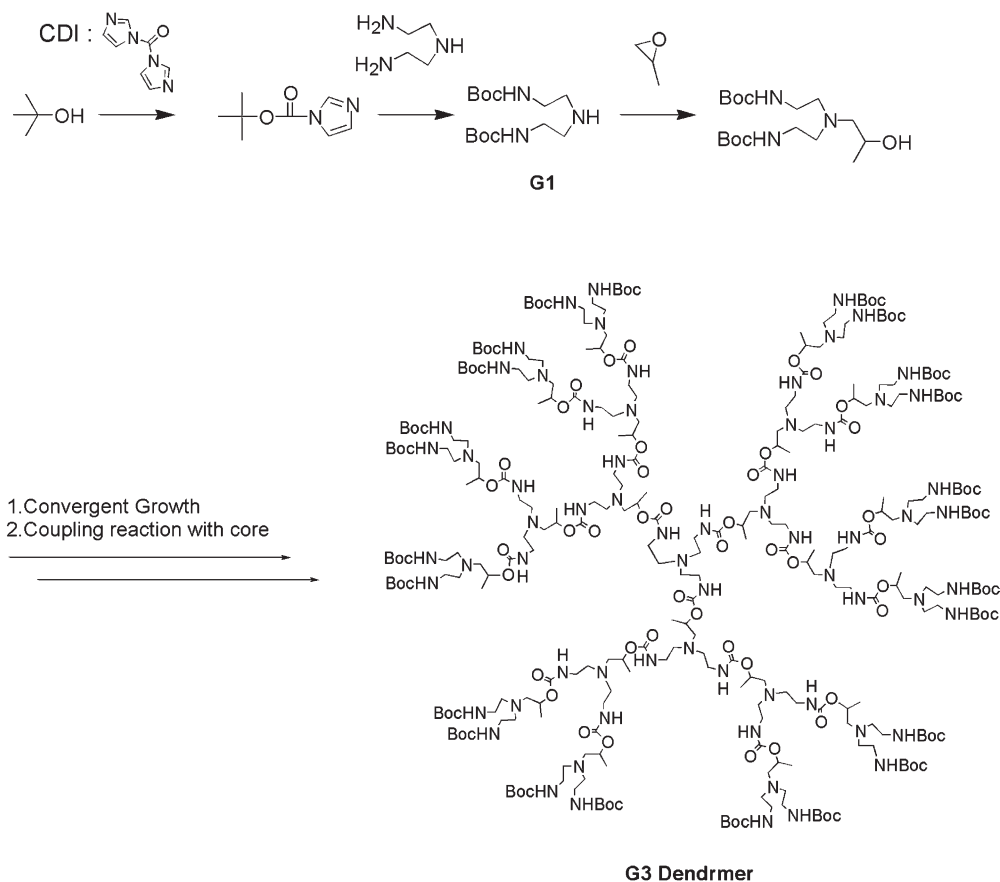
Scheme 18.

functionalized dendrimers especially in some specific conditions such as acidic/basic or physiological conditions.

One of the aims in the field of utilization of dendritic structure for the molecular dynamics seems to be the study on the photochemistry of dendritic photoresponsive molecules such as stilbenes or azobenzenes. Dendrimers with stilbene/azobenzene placed in the core are unique photoresponsive systems since controlling a small conformational change by photoexcitation may be important for creating a macromolecule with a new function, i.e. transfer and amplify the small change in order to regulate change of their whole structure in a precise manner. These systems are interesting not only as candidates for the storage of light energy but also as model systems mediating the conversion of light into other forms of energy. Following points were considered for designing the photoresponsive dendrimers. (1) *Dendrons*: dendrimers can offer the specific environment, not only gives simple bulky substituent effects, but also a voids in the dendrimer interior which is more distinct in water than in organic solvents, when the dendrimers have hydrophobic interior and hydrophilic outside. Polyester or polyamide dendrimers, which are usually synthesized by divergent methods, are not suitable for the purpose of study of photochemical events due to chemical instability. Thus, poly(arylether) dendrons, called Fréchet-type dendrons, were used for designing photoresponsive dendrimers.

Fréchet-type dendrons, prepared by convergent method [105,106], are relatively readily accessed and chemically stable associated with the ether bonds, and are also known to serve the intramolecular singlet energy transfer system. (2) *Location of a chromophore*: to study the dendrimer effect on the behaviors of photoresponsive chromophore, such as stilbene or azobenzene, one chromophore should be placed at the core moiety of the dendrimer. When the multi chromophore molecules are at periphery or in branching units, photochemistry will become more complex and unclear, although it will be a challenging molecule for the study of co-operative effect among photoresponsive chromophores.

3.3. Stilbene dendrimers

The photochemical and photophysical behavior of stilbenes is well-understood and became an important field due to the large number of their practical and potential applications. However, the photoisomerization of stilbenes with large molecular weights like dendrimers was still obscure until quite recently [107,108–111,114–117]. Furthermore, the detail of photochemical behaviors of stilbene core in dendritic molecules is still of interest. Although the azobenzene dendrimers, where *trans*-azobenzene dendrimers undergo isomerization to give *cis*-isomer,
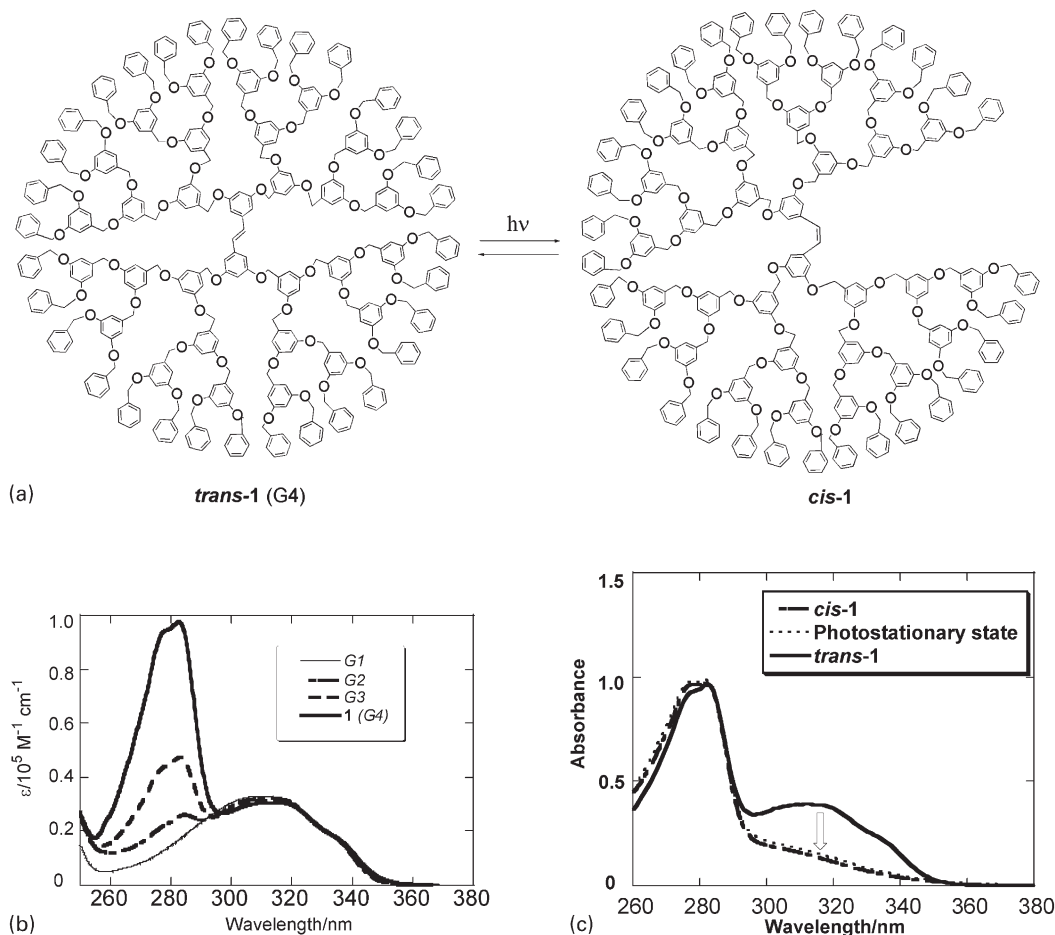
Fig. 6. (a) Photoisomerization of *trans*- and *cis*-stilbene dendrimers **1** (G4). (b) Absorption spectra of stilbene dendrimers G1–G4 in THF solution at room temperature. (c) Absorption spectra of *trans*- and *cis*-**1** and the isomer mixture at the photostationary state on irradiation with 330 nm light in THF at room temperature.

have been reported in many reports as described below, azobenzene does not emit fluorescence and therefore, the dynamic behavior in excited state could not be studied. In this context, a series of stilbene centered dendrimers, having benzyl–ether dendrons were prepared (Fig. 6(a)) [107]. Unlike isomerization of azobenzenes, photoisomerization of C=C double bond usually cannot take place by inversion mechanism, which does not need large volume change at the transient state, but can occur by rotation around the double bond [20]. However, Hula–Twist (H–T) mechanism, postulated by Liu and Hammond, with regard to *cis–trans* isomerization in highly congested media at low temperature or in protein, can be operating [69].

The environment of stilbene in stilbene dendrimers is also highly congested. Therefore, stilbene dendrimers can be considered as appropriate molecules to study the new photochemical isomerization mechanism. Fig. 6(b) shows the absorption spectra of the G1–G4 stilbene dendrimer in THF at room temperature. All dendrimers exhibited the similar absorption spectra at 300–350 nm with the absorption maximum at 310 nm due to the stilbene core. The dendrimers with stilbene core emit fluorescence with high

quantum efficiency (Table 1). In addition, even the G4 dendrimer **1** with a molecular weight as high as 6548 underwent isomerization around C=C double bond within excited singlet state lifetime (Table 1).

The isomer ratio at the photostationary state was determined starting from both pure *cis*- and *trans*-isomers and was [*trans*]/[*cis*] = 5/95 for G4 dendrimer **1** (Fig. 6(c)) [108]. G1 stilbene dendrimer fairly underwent photocyclization reaction from the *cis*-isomer to give dihydrophenanthrene type compound. The photocyclization reaction does not take place in higher generation dendrimers probably due to the steric effect of the bulky dendron groups at meta position.

Table 1
Quantum yields and fluorescence lifetimes of G1–G4 stilbene dendrimers

	Φ_f	$\Phi_{t \to c}$	τ_s/ns (O$_2$)	τ_s/ns (Ar)
G1	0.43	0.32	3.2	9.7
G2	0.46	0.32	3.5	9.3
G3	0.43	0.29	4.1	9.4
G4	0.45	0.24	5.2	9.7

The fluorescence excitation spectra of G1 to G4 dendrimers are similar to the absorption spectra of the corresponding dendrimers, indicate that the peripheral dendron groups could induce fluorescence emission from the stilbene core. The relative intensity of the fluorescence excitation spectrum at 280 nm becomes larger in higher generation dendrimers because the energy transfer efficiency from the surrounding dendron to the stilbene core decreased in higher generation, i.e. increasing dendrimer size. The occurrence of energy transfer from the dendron to the stilbene core by dipole–dipole interaction to produce fluorescence emission from the core moiety since the peripheral dendron groups and stilbene core have no π conjugation, one could explain. The efficiencies of energy transfer process from the dendron to the core were estimated to be 0.81 and 0.34, respectively, for the G3 and G4 dendrimers. The fluorescence lifetimes of *trans*-G1 to G4 dendrimer **2** under oxygen atmosphere are smaller than those under argon atmosphere (Table 1). In addition, the fluorescence lifetime under argon is almost the same among the G1–G4, whereas the fluorescence lifetime under oxygen is slightly different depending on the dendrimer generation. Thus, the singlet lifetimes are 3.2, 3.5, 4.1 and 5.2 ns for *trans*-G1, G2, G3 and **1** (G4), respectively, under oxygen. The result indicates that the higher generation dendrimer suffered less from oxygen quenching ($k_q = 0.9 \times 10^{10}$ M^{-1} s^{-1} for *trans*-G4) than that of the lower generation dendrimer ($k_q = 2.3 \times 10^{10}$ M^{-1} s^{-1} for *trans*-G1) probably due to the bulky dendrons.

The singlet lifetimes, the temperature effect on the lifetimes, and the fluorescence quantum yields were almost the same among the G1–G4 dendrimers. Therefore, the dendron groups do not seem to influence the fluorescence properties or the *trans* → *cis* photoisomerization of the stilbene core. The photoisomerization of the higher generation stilbene dendrimer takes place not by one-bond 180° rotation around the C=C double bond but by another mechanism, with a volume-conserving process, since the isomerization of one-bond rotation around the C=C double bond requires a large volume change in the higher generation dendrimer, which cannot possibly take place within the singlet lifetime. Thus, the volume-conserving process seems to be needed for the isomerization of stilbene dendrimers especially in higher generations. For the stilbene dendrimers, a volume-conserving photoisomerization mechanism such as the H–T [67–71], rather than the conventional 180° rotation around C=C double bond, was proposed according to the fluorescence and isomerization experiments (Fig. 7).

The photochemistry of 3,3′,5,5′-tetramethoxystilbene (TMST) was also studied as a zeros generation of stilbene dendrimer [109]. *trans*-TMST underwent *cis*–*trans* isomerization on UV irradiation. However, *cis*-TMST efficiently underwent a photocyclization reaction to give a dihydrophenanthrene-type intermediate, followed by oxidation to give tetramethoxyphenanthrene, but the isomerization to the
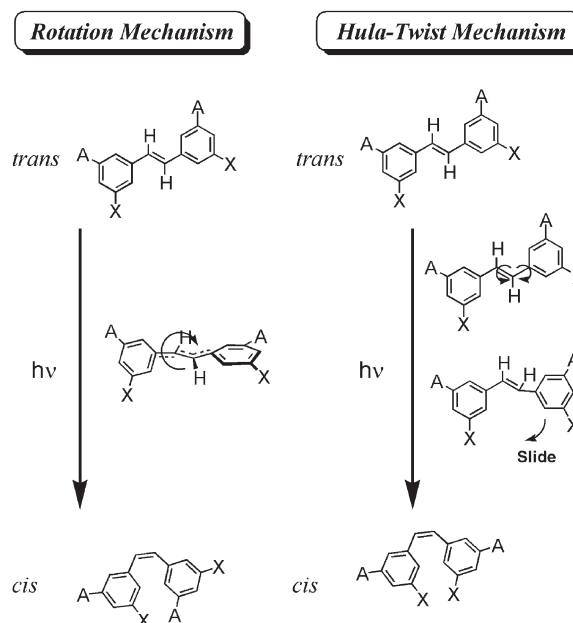

Fig. 7. Proposed molecular movement along the *trans*–*cis* photoisomerization by one-bond rotation and Hula–Twist mechanism.

trans-TMST did not practically take place, as revealed by NMR study as well as isolation and preparation of the pure photoproduct.

By means of the time resolved transient grating method, the energy-releasing processes and conformational changes upon photoisomerization of the same stilbene dendrimers were studied [110]. For all G0 (TMST) to G4 stilbene dendrimers, the excited triplet state with the lifetime of 50 ns was observed. From the time-resolved experiments and the molecular volume changes, it was found that the conformational change completes with the decay of the T1 state for G0–G2, whereas the dynamics are slightly slower for G4 of the thermal process (80 ns) than the triplet lifetime (50 ns) due to the conformational change for the large dendron part. In addition, a large conformational change is suggested by the large difference in the diffusion coefficients for *trans*-G4 and *cis*-G4 [110].

By introduction of the hydrophilic groups at the periphery in hydrophobic dendrimer, one can make a WSD like uni-molecular micelles. In this connection, the photochemical behaviors of stilbenes in that special environment should be interesting. A WSD with a photoresponsive core, such as stilbenes or azobenzenes, may be a model compound for a photoreversible biomolecule and a photoreversible unimolecular micelle. In this context, WSDs with carboxylate-terminated dendron groups were synthesized (Fig. 8(a)). Their photochemical behavior of WSDs in water, where the core of the higher generation dendrimer should be isolated from the outside water, has been studied [111]. Figure 8(b) shows the absorption spectra of the G1 to G3 WSDs. Unlike stilbene dendrimers **1** and their series [109] in organic solvent, the fluorescence maxima for the WSDs appeared at different wavelengths
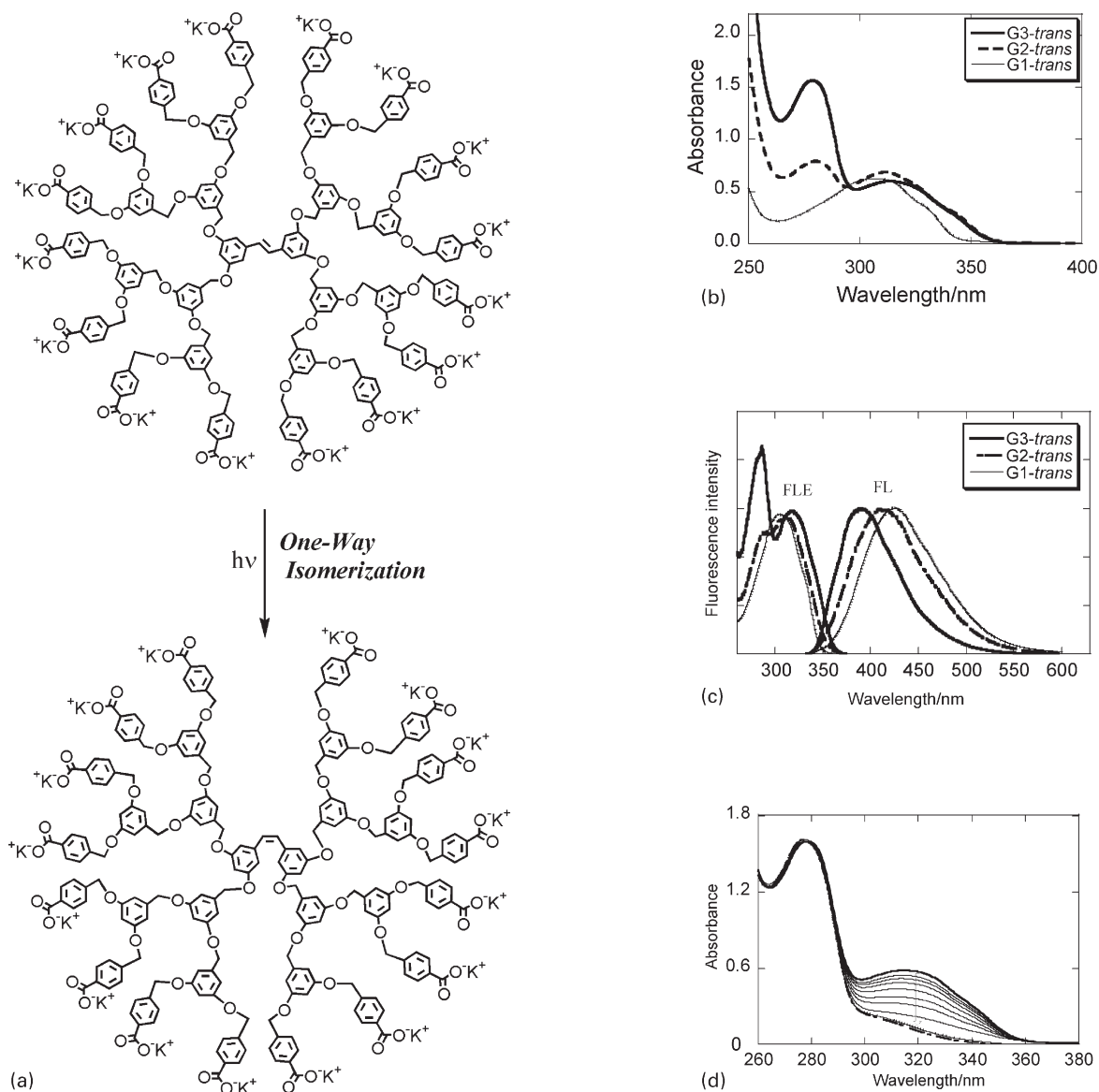
Fig. 8. (a) Photoisomerization of water-soluble stilbene dendrimers G3. (b) Absorption spectra of water-soluble stilbene dendrimers G1–G3. (c) Normalized fluorescence (FL) and fluorescence excitation spectra (FLE) of water-soluble stilbene dendrimers G1–G3 in KOH aqueous solutions. (d) Change in the absorption spectra of *trans*-G3 on irradiation with 330 nm light in KOH aqueous solution.

depending on the generation (Fig. 8(c)) in water. The fluorescence maxima from the stilbene core of the WSDs blue-shifted in higher generation (λ_{max}: 424, 411 and 389 nm for G1, G2 and G3, respectively). These results suggest that increasing generations of WSDs cause decreases in the interaction between the stilbene core and water due to the hydrophobic dendron groups, which diminishes the stabilization of the excited state of the stilbene core by solvent water. On UV irradiation in aqueous solution, the G3-WSD underwent an unusual one-way *trans*-to-*cis* photoisomerization to give almost 100% of the *cis* isomer in the photostationary state, which was revealed by changes in the absorption spectra (Fig. 8(d)). Stilbene usually undergoes a photochemical mutual *cis–trans* isomerization to give a photostationary mixture of *trans*-

and *cis*-isomers with prolonged irradiation. However, there are exceptions to this one-way isomerization. One of them is the photochemical one-way *cis*-to-*trans* isomerization for stilbene-like compound with an anthracene ring instead of one of the phenyl rings. Thus, styrylanthracene undergoes one-way isomerization with considerably high quantum efficiency [34]. Another example of one-way isomerization is the *trans*-to-*cis* one-way isomerization for hydrogen bonded compounds [112,113]. In this case, only the *cis*-isomer forms intramolecular hydrogen bonds to accelerate the deactivation from the *cis*-form without undergoing isomerization to the *trans*-isomer. Water-soluble stilbene dendrimers WSDs does not have any intramolecular hydrogen bonding at the core stilbene, or any substituent to change the potential energy surface to induce isomerization

in a specific way. Thus, the occurrence of the one-way isomerization in G3-WSD must be caused by the surrounding dendron groups.

Due to the hydrophilic peripheral carboxylate anion groups and hydrophobic interior, the molecular structure of G2 and G3 becomes more compact by intramolecular hydrophobic interaction, and therefore, the average distance between the dendron group and core stilbene becomes shorter to accelerate the energy transfer from the dendron groups to the core stilbene. Because of the compact structure in water, a structural change from the *cis* isomer might have a higher steric effect, inhibiting the *cis*-to-*trans* photoisomerization.

Addition of salt (KCl) to the aqueous solution of the water-soluble stilbene dendrimers affected the fluorescence and fluorescence excitation spectral changes. This is probably due to decrease of the interactions between the cores of the dendrimers and solvent water [114]. The intramolecular energy transfer from the surrounding dendron groups to the stilbene core in the G2 dendrimer changed from 49% to ca. 100% by the addition of salt.

The other interesting feature is the possibility of using the molecule as a photoresponsive unimolecular micelle, which can incorporate hydrophobic molecules inside in G3, and, upon photoirradiation, *trans*-G3 undergoes a one-way *trans*-to-*cis* isomerization to give exclusively *cis*-G3. *cis*-G3 should have a different structure from global G3, and may exhibit different hydrophobic and hydrophilic properties from *trans*-G3.

The other dendrimers, having a stilbenoid compound in the core have also been used as model systems to understand the dynamic processes of oxygen in large molecules. The photoresponsive 1,3,5-tristyrylbenzene dendrimers were prepared (G4 dendrimer, Fig. 9(a)), as molecules appropriate for this study. The advantage of using the tristyrylbenzene dendrimers is that the production of singlet oxygen and the dynamic quenching process by oxygen can be revealed by the quenching rate of the singlet state measured with each generation of dendrimer. 1,3,5-Tristyrylbenzene seems to be an appropriate molecule as a dendrimer core because of its long-lived excited singlet state and to observe the triplet state after quenching the singlet state by oxygen. The absorption spectra of the series of 1,3,5-tristyrylbenzene dendrimers are shown in Fig. 9(b). Almost the same fluorescence spectra among the generations are observed, while the fluorescence excitation spectra were different in the shorter wavelength region (Fig. 9(c)) due to singlet energy transfer from the peripheral dendron groups to the core as shown in other stilbene dendrimers. For the G0, G2, and G4 1,3,5-tristyrylbenzene dendrimers, control of the efficiency of photoisomerization by oxygen was demonstrated [115]. On UV irradiation, the absorption spectra of the dendrimers changed as shown in Fig. 9(d). Due to volume-conserving isomerization mechanisms, the large dendron did not actually affect the

photochemistry itself, but may affect the mobility of the molecules in corporate into the dendrimers.

The surrounding benzyl-ether type dendron groups in stilbene dendrimers are not π-conjugated with the stilbene core but affected the photochemical behavior of the core moiety. The next interest in the dendric effect on the stilbene dendrimers is to investigate the photochemical processes of dendrimers where conjugation is not localized in the stilbene core but can be spread throughout the large molecule. In this context, stilbene dendrimers with polyphenylene as dendron groups were synthesized (Fig. 10(a)) [116]. The UV absorption spectra of stilbene and the polyphenylene dendrimers are shown in Fig. 10(b). The absorption edges among the each generation of the polyphenylene dendrimers are almost the same because the absorbance in the longer wavelength region is assigned to the stilbene core. The extinction coefficient at 250–320 nm increase in higher generation of dendrimer due to the peripheral polyphenylene dendrons. *trans*-Isomers of polyphenylene dendrimers exhibited *trans*–*cis* photoisomerization. The fluorescence spectra for the dendrimers are shown in Fig. 10(c) and fluorescence quantum yields for the G1 and the G2 polyphenylene dendrimers are 0.69 and 0.64, respectively, which are more than 10 times higher than that of *trans*-stilbene ($\Phi_f = 0.04$) [21]. The *cis*-isomer of the G2 polyphenylene stilbene dendrimer underwent one-way *cis*-to-*trans* isomerization at 77 K in a rigid solvent glass. The result clearly indicates that a volume-conserving isomerization mechanism is operating [117] for the polyphenylene dendrimers.

3.4. Azobenzene dendrimers

Photoisomerization of azobenzenes is remarkably clean reaction. The *trans*-isomer is thermodynamically more stable than the *cis*-isomer, obtained by UV light irradiation, and can be converted back to the *trans*-isomer by photoexcitation and thermally in the dark. In addition, the two isomers exhibit different absorption spectra. Azobenzene and its analogues are known as the other best-understood photoresponsive molecules and play an important role for a tremendous number of functionalized molecules due to their efficient photo/thermal isomerization properties.

The first azobenzene-centered dendrimers were reported in 1997 [118–125]. The absorption of infrared light (1597 cm^{-1}) followed by multi-photon intramolecular energy transfer from the surrounding dendron groups to the azobenzene core accelerated *cis*-to-*trans* isomerization in 3,3′,5,5′-tetra substituted azobenzene dendrimers [119, 120]. For G0, G1, and G3 azobenzene dendrimers, the thermodynamic parameters, such as activation energy of thermal *cis*-to-*trans* isomerization of azobenzene dendrimer compared to that of the low molecular weight azobenzene, were also reported [121]. The other azobenzene-centered dendrimers having benzyl ether-type dendrons are also reported by McGrath and cowokers [122–125].
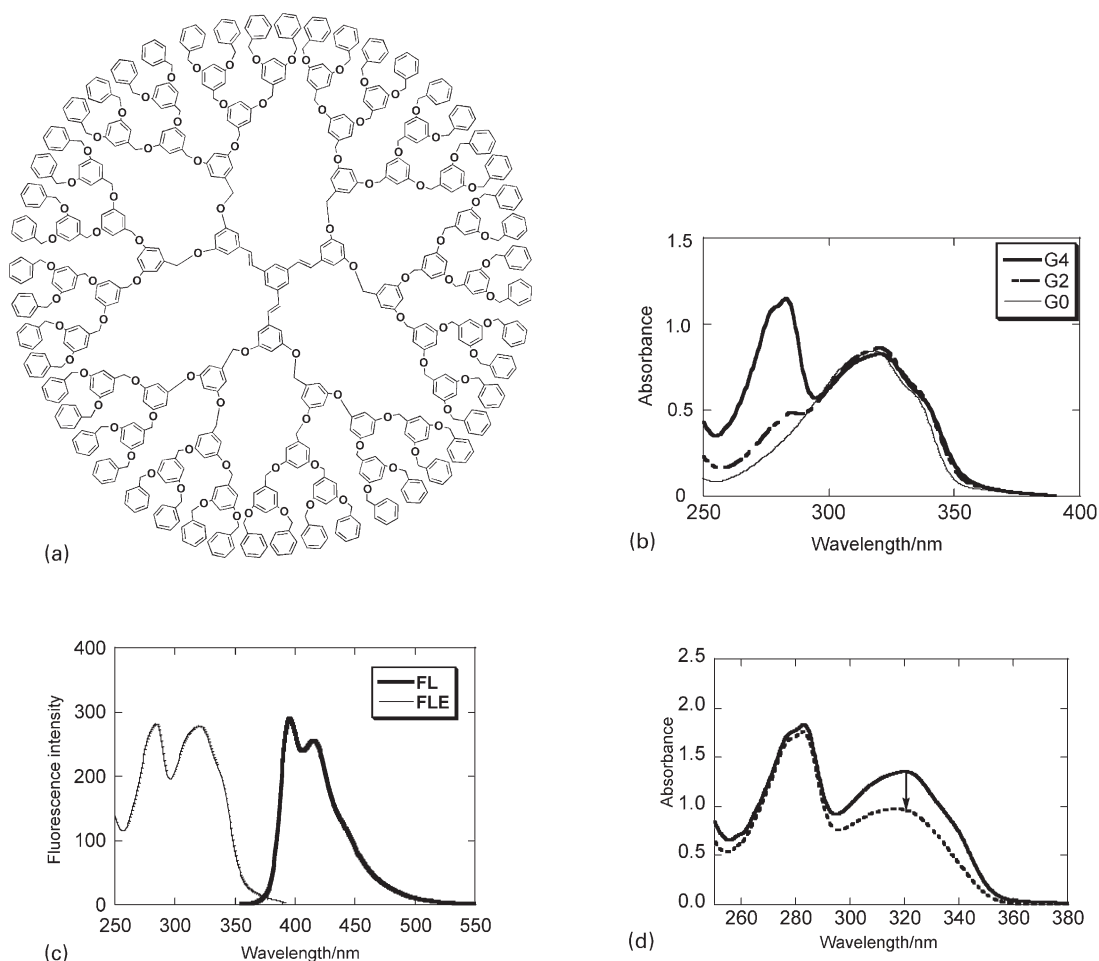
Fig. 9. (a) All-*trans*-tristyrylbenzene dendrimer (G4). (b) Absorption spectra of tristyrylbenzene dendrimers. (c) Fluorescence (solid line) and fluorescence excitation spectra (thin line) of G4 in THF. (d) Change in the absorption spectrum of G4 tristyrylbenzene dendrimer on irradiation with 330 nm light in THF: before (solid line) and after (dotted line) irradiation.

Since azobenzene are easy to be functionalized, many azobenzene dendrimers where the azobenzene units placed in the dendron group were synthesized [126–135]. As two or more azobenzene units are included in one molecule, the conformation pattern triggered by photoirradiation becomes much more complex than that in azobenzene-cored dendrimers. Therefore, many dendrimers with azobenzene-dendron were prepared mostly for use in the material science rather than for studying the photochemical behavior of azobenzene in dendritic macromolecules.

4. Features of dendrimer photochemistry

As already been mentioned in this article, one could prepare photofunctionalized dendrimers with different molecular weight depending on the generation. Furthermore, hydrophobic and hydrophilic nature of the dendrimers in their inner part and the outer part can be easily changed by the introduction of the appropriate substituents. Thus, the dendrimers can serve as an interesting environment to explore the molecular movement and novel photochemical

reaction affected by the so-called cage effect and can mimic the environments in large molecules such as proteins, polymers, micelles and vesicles (Fig. 11). The oxygen quenched the excited singlet state of the stilbene core of the dendrimers probably producing the excited state singlet oxygen. When the experiments are performed in water soluble dendrimers, the fate and the molecular dynamics of the singlet oxygen inside the dendrimer hydrophobic environment and the diffusional process going out from the hydrophobic dendrimer interior to the hydrophilic bulk water can be easily explored (Fig. 12). The dendrimers having chromophore with energy gradient from inner sphere to the outer sphere or vice versa can be prepared to mimic the efficient antenna for light capture and energy transfer molecular assemblies. The appropriate design can also make drug delivery system incorporate and transport important drugs.

This review contains a limited number of dendrimer chemistry and we can understand that there are many interesting chemical reactions and chemical and physical properties and application, which have already been reported as well as been studying. However, the author
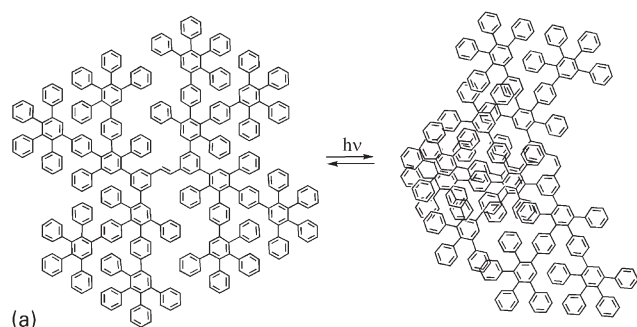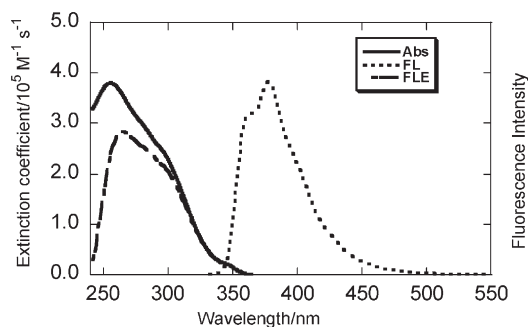
(a)
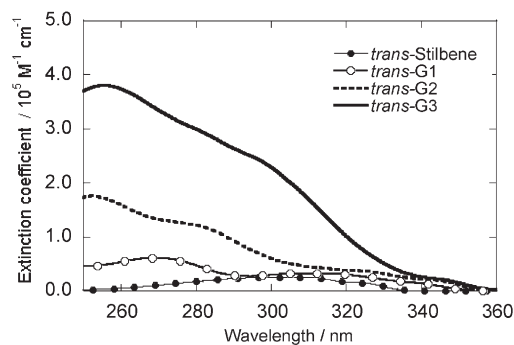
(b)

(c)

Fig. 10. (a) Photoisomerization of *trans*- and *cis*-polyphenylene dendrimers G2. (b) Absorption spectra of stilbene and G1–G3 polyphenylene dendrimers. (c) Absorption, fluorescence and fluorescence excitation spectra of G2 in chloroform under Argon.
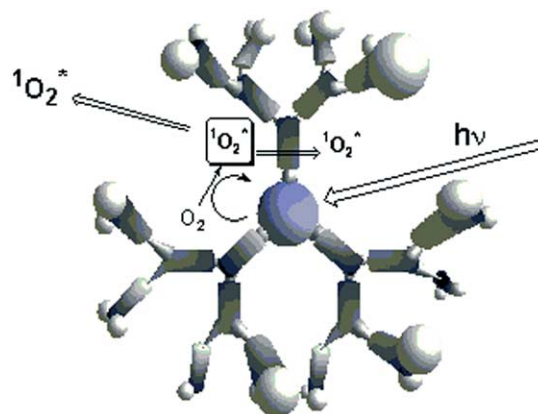

Fig. 12. Producing of singlet oxygen inside the dendrimer in water.

realized that isomerization around the double bond as one of the basic process in photochemical and thermal processes can serve as a wide variety of the application purposes as well as to find new concepts for basic and fundamental physical organic chemistry. The small change of the chemical chromophore may amplify the molecular change as the large molecular structural change. The ultrafast structural change induced by pulsed laser may induce the ultrafast change of the chemical chromophore, but the structural change of the surrounding dendron parts may take place rather slowly and therefore the whole molecular structural changes can be followed by using appropriate dendrimer molecules and experimental setup. Furthermore, the environmental change induced by molecular structural change by photon can change the color of the molecule and, therefore, one can prepare novel photochromic large molecules.

5. Conclusions

The considerably fast molecular structural changes of dendrimers with large molecular size induced by photon and recent advances of dendrimer syntheses in both divergent and convergent approaches were discussed. Azobenzene-containing dendrimers may have the potential for many
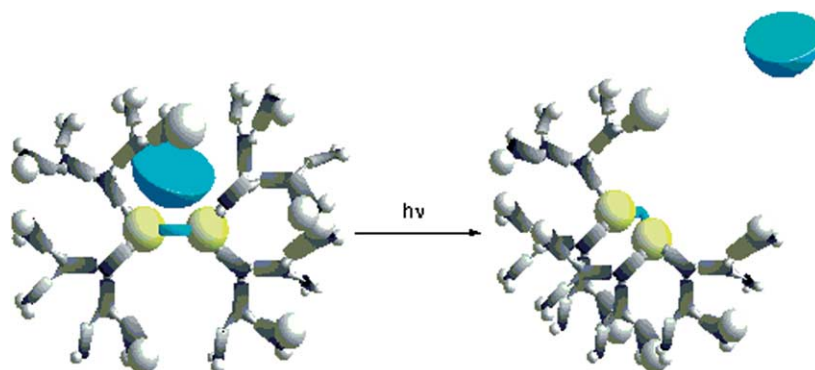

Fig. 11. Schematic illustration of the photochemical regulation between catch and release of molecules by change of structure and hydrophobicity of water-soluble dendrimers with photoresponsive core.

different types of application aspects. The stilbene dendrimers are discovered to be useful molecules to study the dynamic behavior and the effect of surrounding dendron groups by monitoring their fluorescence and measuring the efficiency of isomerization, since the stilbene is the basic compound for the study of photochemical structural changes and its photochemistry and photophysics of stilbene were fully discovered. The photochemical *cis–trans* isomerization of dendrimer molecules may be related to processes occurring in photoresponsive biomolecules such as rhodopsin and phytochrome. One can expect to prepare tailor-made biopolymers which can be regulated by light energies, when the research projects for photoresponsive dendrimers have been appropriately extended and progressed.

The isomerization of stilbene dendrimers substituted at the meta position takes place within the lifetime of the excited singlet state (ca. 10 ns). One can prepare compounds capable to undergo isomerization much faster when the dendron group is introduced at the *ortho* position or *para* position. In this case, the C=C double bond may undergo isomerization 10–100 times faster than the stilbene dendrimer having the dendron group at the meta position. Then one can expect the ultrafast structural change in the excited singlet state followed by the rather slow process of the surrounding dendron group. In addition, WSDs having photoresponsive core such as stilbene or azobenzene may be used as a drug delivery polymers.

The quenching experiments of the dendrimer core by molecular oxygen provide us with an interesting aspect regarding to the production and behavior of excited state singlet oxygen as well as the mobility of oxygen in the congested molecular environment. In photodynamic therapy, singlet oxygen is sometimes mentioned as an important active species. Therefore, a study of the efficiency of excited state oxygen would be interesting to carry out in order to explore the reactive species of oxygen in large dendritic molecules, in connection with the biological importance of the reactive oxygen species.

The study of the photoisomerization of stilbene dendrimer revealed that even the dendrimer compounds with molecular weight as high as 6500, regardless to whether they are dissolved in water or organic solvent, underwent *cis–trans* isomerization. In this case the change of the molecular structure of large denrimer molecules was regulated by only one photon and therefore, this finding can be developed for the construction of molecules to amplify the photon effect by transferring the structural change of the small photoresponsive molecule to a change of the whole structure of the large dendrimer molecule.

Acknowledgements

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Atsuya Momotake was born in 1971 (Tokyo, Japan), graduated from the Faculty of Science, Toho University in 1994, and received his PhD from Chiba University in 1999. After a six-month stay in the same group as a Research Associate, he moved to the MCP Hahnemann University in Philadelphia (Drexel University, College of Medicine) where he worked as a Postdoctoral Fellow from 2000 to 2002. He then moved to the University of Tsukuba, where he is currently working with Professor Tatsuo Arai as a Postdoctoral Fellow from 2002 to 2004 and as a Research Associate from 2004. His research interests include synthesis and photochemical properties of dendrimers and caged compounds.

Tatsuo Arai was born in Kumagaya (Saitama Prefecture) in Japan in 1953. He received his BSc degree in 1976 at Tohoku University and his PhD degree in 1981 at the University of Tsukuba. He worked as a research associate, assistant professor, and associate professor in the Department of Chemistry, University of Tsukuba. He was promoted to full professor in 1997. He is presently a professor of Graduate School of Pure and Applied Science and Technology, University of Tsukuba. From 1983 to 1984 he worked at the Max-Planck Institute for Radiation Chemistry in Mulheim/Ruhr, Germany as an Alexander von Humboldt Fellow. He was the winner of the 2002 Japan Photochemistry Association Award. His research interests include photochemistry and the excited state dynamics of dendrimers and hydrogen-bonded compounds, as well as the dynamics and control of reactive intermediates produced by photoirradiation.