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LETTERS

Dendritic fullerenes (C_{60}) with photoresponsive azobenzene groups

Kwang-Yol Kay,[a,*] Ki-Jong Han,[a] Yong-Jae Yu[a] and Young Dong Park[b]

[a]*Department of Molecular Science and Technology, Ajou University, Suwon 442-749, South Korea*
[b]*Department of Chemistry, Ajou University, Suwon 442-749, South Korea*

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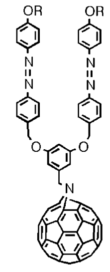
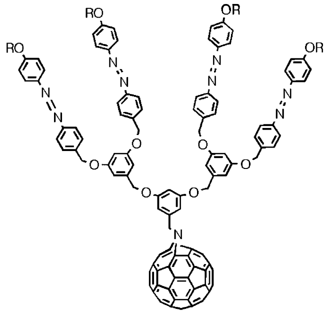
Abstract—Fullerene-cored dendrimers bearing up to eight photoisomerizable azobenzene groups in the periphery have been synthesized as potential photoswitches and spectroscopically characterized. © 2002 Elsevier Science Ltd. All rights reserved.

Design and synthesis of dendrimers with multifunctionality has attracted much attention due to their unlimited possibility for fundamental new discoveries and practical applications.[1–15] Among the various electro- and photoactive chromophores utilized for dendrimer chemistry, both fullerene (C_{60}) and azobenzene groups appear to be versatile building blocks, and at present a growing interest is developing in fullerene-functionalized[14,16–24] or azobenzene-functionalized[25–29] dendrimers. In addition, Sano and Shinkai et al. reported on synthesis and film properties of a C_{60}–azobenzene derivative with an ammonium group to obtain stable monolayers.[30] In line with these aspects, we report herein the synthesis of fullerene-cored dendritic molecules **1**, **2** and **3** bearing up to eight photoisomerizable azobenzene groups in the periphery as potential photoswitches.

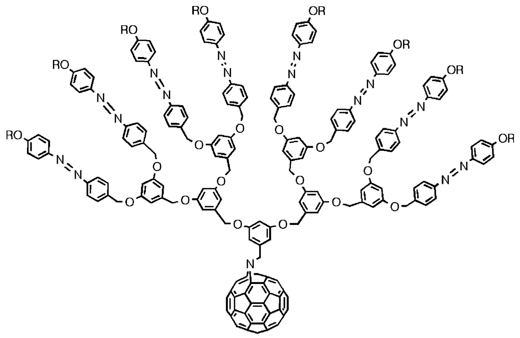
Photoresponsive dendrimers **1**, **2** and **3** of the first, second and third generations were prepared by a typical Fréchet's convergent method[31] in which the reaction of azobenzene derivatives [Gn]-Br with the monomer 3,5-dihydroxybenzyl alcohol repeats for the dendrons of higher generations, and then the appropriate dendritic azides [Gn]-N_3 react with C_{60} in chlorobenzene at the final step[17] to give the corresponding dendritic fullerenes **1**, **2** and **3**, respectively. Every step of the reaction sequence proceeded smoothly and efficiently to give a good or moderate yield of the product (Schemes 1–3).



1



2 R = C_4H_9



3 R = C_4H_9

Dendritic fullerenes **1**, **2** and **3** are brown-colored solids and prove to be soluble in a variety of organic solvents, unlike C_{60}.[32] They were characterized by ^{1}H, ^{13}C NMR, FAB or MALDI-TOF Mass and elemental analysis.[33] ^{1}H NMR spectra of **1**, **2** and **3** showed very similar patterns of the resonance lines, which shifted downfield from the corresponding resonance lines of the precursor azides **9**, **12** and **15** due to the electron withdrawing influence of the fullerene sphere. The resonances for the exterior azobenzene groups occur at 6.96–7.88 ppm, the

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Keywords: fullerene; azobenzene; dendrimer; absorption spectrum; UV-irradiation; *trans–cis* isomerization; polarized optical microscopy.

* Corresponding author. Tel.: 82-31-219-2602; fax: 82-31-219-1615; e-mail: kykay@madang.ajou.ac.kr

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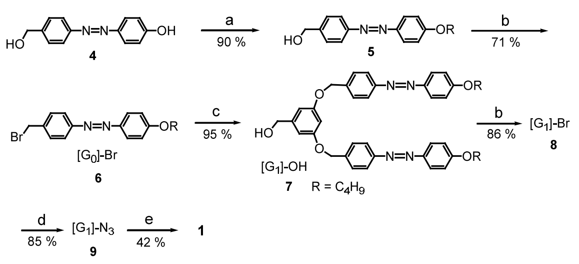
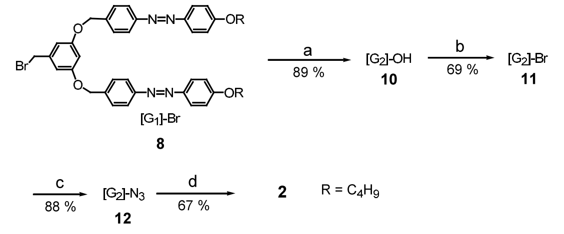
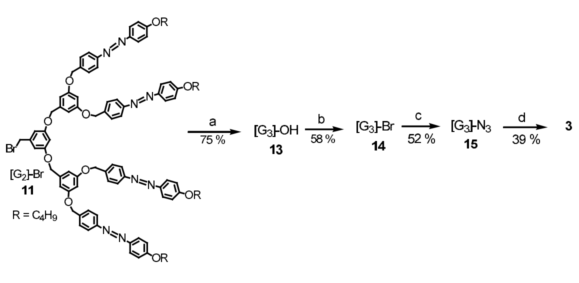
peaks for the aromatic protons of the monomer units appear in the region 6.40–6.77 ppm and the resonances for the methylene protons occur in the region 4.80–5.20 ppm (Ar-O-CH_2Ar), 4.37–4.47 ppm (N-CH_2) and 4.01–4.02 ppm (azobenzene-O-CH_2). Other alkyl chain protons show the resonances in the region 0.98–1.78 ppm. ^{13}C NMR spectra of **1**, **2** and **3** showed almost the same chemical shifts. A set of fullerene nucleus peaks appears in the aromatic region between 133 and 148 ppm and a resonance line of CH_2–N occurs at 68 ppm (Fig. 1). These peaks correspond to the open annulene structure of a monosubstituted C_{60} azafulleroid and agree with the results of Prato and Wudl[34] and Hawker.[17] The remainder of the resonances in the spectrum are due to the aromatic monomer (101–108 and 114–131 ppm) and azobenzene carbons (114–162 ppm) of the dendritic units, appearing as distinct peaks with relatively higher intensity than the peaks of fullerene carbons. The resonances for the aliphatic carbons (O-CH_2 and *n*-butyl) appear at 70, 31, 19 and 14 ppm.



Scheme 1. *Reagents and conditions*: (a) *n*-BuBr, K_2CO_3, DMF, 80°C; (b) CBr_4, PPh_3, $CH_2Cl_2/CHCl_3$ (1:1), rt, 1.5 h; (c) 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, acetone/THF (1:1), reflux, 18 h; (d) NaN_3, CH_3CN/THF (1:1), reflux, 18 h; (e) C_{60}, chlorobenzene, reflux, 24 h.



Scheme 2. *Reagents and conditions*: (a) 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, acetone/THF (1:1), reflux, 18 h; (b) CBr_4, PPh_3, $CH_2Cl_2/CHCl_3$ (1:1), rt, 1.5 h; (c) NaN_3, CH_3CN/THF (1:1), reflux, 18 h; (d) C_{60}, chlorobenzene, reflux, 24 h.



Scheme 3. *Reagents and conditions*: (a) 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-crown-6, acetone/THF (1:1), reflux, 18 h; (b) CBr_4, PPh_3, toluene, 5°C, 0.5 h and then rt, 12 h; (c) NaN_3, THF, reflux, 18 h; (d) C_{60}, chlorobenzene, reflux, 24 h.

Further confirmation of the hybrid dendrimer–fullerene structure was obtained from the IR and UV–vis spectra of **1**, **2** and **3** which were found to contain absorbances due to both the dendrimer and fullerene fragments.[33]

Dendrimers **1**, **2** and **3** all exhibited the expected photoresponsive behavior. For example, dark incubation of a chloroform solution (10^{-5} M) of third generation dendrimer **3** served to maximize the absorption at 357 nm (log $\varepsilon = 5.20$) corresponding to the *trans*-azobenzene chromophore.[35] Irradiation of this solution with 365 nm light resulted in clean photoisomerization to *cis*-azobenzene, as evidenced by a decrease in the absorbance at 357 nm and an increase in absorbance at 437 nm (Fig. 2). A photostationary state was reached within approximately 150 s. Thermal reversion to the original dark-incubated spectrum was observed over the course of approximately 6 h at 293 K in the dark. However, exposure to bright sunlight for a period of only several seconds also effect almost complete reversions to the *trans* isomer. The first and second generation dendrimers **1** and **2** also showed the same trends in *trans–cis* reversible isomerzation phenomena. This indicates that there is no strong steric influence on the *trans–cis* reversible isomerization of **1**, **2** and **3**. In addition, the photoresponsive behavior of the azobenzene is not perturbed by incorporation into fullerene-cored dendritic structure.

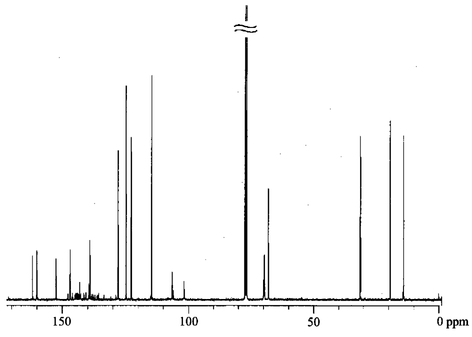


Figure 1. ^{13}C NMR spectrum **3** in $CDCl_3$ at 25°C.

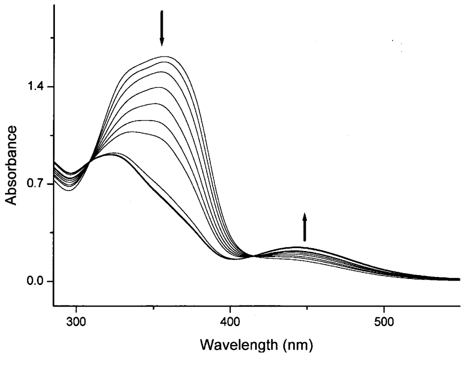


Figure 2. UV absorption spectra of **3** under irradiation conditions (365 nm: 0, 5, 10, 15, 20, 25, 30, 60, 90, 120 and 150 s).

The data of differential scanning calorimetry (DSC) for **1**, **2** and **3** showed high thermal stability. Glass transition temperatures (T_g) of **1**, **2** and **3** were found to be 370, 358 and 348 K, respectively. These values were 45, 33 and 23 K higher than the value 325 K of the previously reported Hawker's benzylether dendrimer with fullerene core,[17] which is also 13 K higher than the T_g value (312 K[36]) of the corresponding dendrimer without fullerene core indicating the strong influence that azobenzene and fullerene portions have on the overall properties of the hybrid molecules **1**, **2** and **3**.[37] However, the T_gs of [G_1], [G_2] and [G_3] dendrimers decrease with increasing generations.

Polarized optical microscopy suggests that the films derived from **1**, **2** and **3** are uniform and isotropic (nonbirefringent), showing no mesophase upon heating or cooling between 30 and 270°C. Therefore, films can be readily fabricated by melt processing. This study has yielded robust, nonscattering glasses which appear indefinitely stable with respect to crystallization. These easily processable solid solutions are suitable materials for further optical studies, which are now under investigation.

Acknowledgements

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33. Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported.
   Selected physical data for **1**: brown solid; mp >280°C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 8H), 7.49 (m, 4H), 6.96 (m, 4H), 6.77 (s, 2H), 6.60 (s, 2H), 5.11 (s, 4H), 4.42 (s, 2H), 4.02 (m, 4H), 1.77 (m, 4H), 1.51 (m, 4H), 1.00 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 161.75, 159.95, 152.34, 146.81, 138.97, 130.50, 128.00, 124.83, 122.90, 114.69 (azobenzene and Ar. monomer C), 107.81, 101.78 (Ar. monomer C), 147.56, 146.17, 145.31, 145.04, 144.82, 144.74, 144.52, 144.44, 144.22, 144.10, 144.03, 144.00, 143.97, 143.65, 143.53, 143.24, 142.58, 142.03, 141.53, 141.46, 140.38, 139.67, 139.58, 139.35, 139.16, 139.09, 138.97, 136.80, 135.49, 134.60, 133.61, 132.70 (fullerene carbons), 69.72 (O-CH_2), 68.05 (N-CH_2), 31.23 (CH_2), 19.21 (CH_2), 13.83 (CH_3); FAB-MS m/z 1389 (M^+), 1448, 720 (C_{60}), 211 (base peak); FT-IR (KBr) ν 3055, 2959, 2932, 2866, 1600, 1503, 1250, 1142, 839 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 261 (5.05), 351 (4.91), 437 (sh, 4.00), 632 (3.39) nm at 10^{-5} M.
   Selected data for **2**: brown solid; mp >279°C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 16H), 7.45 (m, 8H), 6.96 (d, 8H), 6.40–6.70 (m, 9H), 4.80–5.20 (m, 14H), 4.01 (m, 8H), 1.77 (m, 8H), 0.98 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 161.74, 160.07, 152.43, 146.87, 138.95, 130.51, 127.94, 124.81, 122.90, 114.74 (azobenzene and Ar. monomer C), 106.53, 106.16, 101.78 (Ar. monomer C), 147.73, 146.14,

144.95, 144.55, 144.47, 144.39, 144.22, 143.99, 143.94, 143.77, 143.53, 143.33, 143.07, 142.86, 142.74, 142.67, 142.62, 141.42, 140.75, 139.66, 139.60, 139.29, 139.19, 139.00, 138.95, 138.44, 138.13, 137.56, 136.96, 136.21, 135.70, 133.67 (fullerene carbons), 69.70 (O-CH_2), 68.08 (N-CH_2), 31.26 (CH_2), 19.24 (CH_2), 13.85 (CH_3); FAB-MS *m*/*z* 2166 (M^+), 1448, 720 (C_{60}), 261 (base peak); FT-IR (KBr) ν 3058, 2963, 2928, 2870, 1596, 1500, 1243, 1141, 839 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 253 (4.50), 353 (4.96), 435 (sh, 3.82), 637 (3.21) nm at 10^{-5} M.

Selected data for **3**: light brown solid; mp >272°C (dec.); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 32H), 7.49 (m, 16H), 6.97 (m, 16H), 6.40–6.70 (m, 21H), 4.85–5.15 (m, 28H), 4.40 (m, 2H), 4.02 (m, 16H), 1.78 (m, 16H), 1.52 (m, 16H), 0.99 (m, 24H); ^{13}C NMR ($CDCl_3$) δ 161.76, 160.03, 152.30, 146.85, 139.01, 130.54, 127.96, 124.81, 122.78, 114.70 (azobenzene and Ar. monomer C), 106.53, 106.44, 106.16, 101.79 (Ar. monomer C), 147.69, 146.07, 144.90, 144.59, 144.40, 144.35, 144.19, 144.00, 143.90, 143.72, 143.56, 143.28, 143.07, 142.78, 142.71, 142.63, 142.58, 141.38, 140.70, 139.66, 139.55, 139.30, 139.15, 139.01, 138.93, 138.39, 138.10, 137.53, 136.91, 136.16, 135.67, 133.63 (fullerene carbons), 70.00, 69.73, 69.66 (O-CH_2), 68.06 (N-CH_2), 31.26 (CH_2), 19.23 (CH_2), 13.85 (CH_3); MALDI-TOF MS did not show M^+ peak; FT-IR (KBr) ν 3060, 2956, 2931, 2872, 1599, 1500, 1252, 1153, 1140, 839 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 252 (5.16), 357 (5.20), 437 (sh, 4.20), 633 (3.27) nm at 10^{-5} M.

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35. The molar absorptivity of **3** is relatively higher than the values of **1** and **2**. However, the reason for this synergistic effect of eight azobenzene groups in **3** cannot be clearly explained yet. We are still working on this question.
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37. In this preliminary communication, further comparison of these T_g values of **1**, **2** and **3** with the precursors **9**, **12** and **15** was not made, but will be reported elsewhere together with other film properties.