Photoresponsive Dendrimers: Syntheses and Characterizations of Anthracenes Bearing Dendritic Substituents

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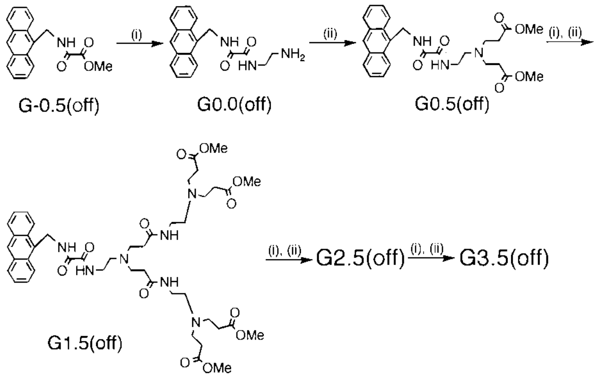
A new photoreactive anthracenyl dendron undergoes a reversible photocyclization to form a dendrimer.

Dendrimers that respond to environmental stimuli are of current interest due to their relevance to control of their basic physical and chemical properties such as self-assembly,[1] liquid crystallinity,[1c,2] intramolecular singlet energy transducer,[3] biological recognition,[4] and encapsulation.[5,6] In particular, there is an increasing focus on developing applications for photoresponsive dendrimers which have intramolecular photo-switch.[7–11] For example, Vögtle et al. reported on the synthesis of dendrimers containing azobenzene units in the periphery toward photoswitchable dendritic hosts.[7] Aida et al. have been reported that the polyuracil dendrimers can be intramolecularly locked via photoinduced dimerization of the uracil units and act as a multidentate ligand for a rare-earth metal ion.[8,12] Recently, we have described dechalcogenation reaction of dendrimer dichalcogenides upon irradiation.[9] In contrast, structural control of dendrimers via intermolecular photochemical reactions has not been well explored. Anthracene derivatives are candidate materials for application in the areas of optical information storage and optical switching systems because of their facile and reversible photodimerization characteristics. However, dendrimers incorporating the photoreactive anthracene moiety have never been reported. During our studies on the structural control of dendrimers,[9] we found that anthracene moieties efficiently acted as a photoresponsive switch of the dendritic architecture. This paper describes the syntheses and characterizations of poly(amide amine) dendrons having an anthracene moiety at the focal point, although a dendrimer having interior switchable moieties is quite rare.[8,9,10] In particular, the first example of a photoresponsive dendrimer by the use of intermolecular reaction is reported.

Dendrons G1.5(off) – G3.5(off) were prepared using the methodology developed by Tomalia and co-workers (Scheme 1).[13] A focal point of dendron, compound G0.0(off), was obtained by the reaction of compound G0.5(off) with ethylenediamine. Subsequently, treatment of G0.0(off) with methyl acrylate produced a dendron G0.5(off) in 100% yield. This two-step process can be repeated to prepare G1.5(off), G2.5(off), and G3.5(off) in 79, 40, and 37% yield, respectively. The structures of G1.5(off), G2.5(off), and G3.5(off) were confirmed by ^{1}H, ^{13}C NMR spectroscopies, elemental analysis, and MALDI-TOF MS.[14] The MALDI-TOF spectrum and the size-exclusion chromatography (SEC) trace of dendron G3.5(off) were shown in Figure 1 (a) and (b).[15]



Scheme 1. Syntheses of dendrons G1.5(off) - G3.5(off). Reaction conditions: (i) ethylenediamine (50 equiv); (ii) methyl acrylate (10 equiv), MeOH.

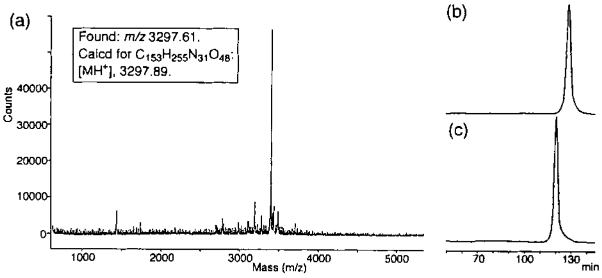
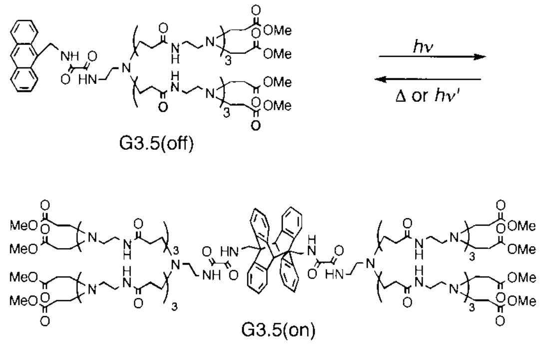


Figure 1. (a) MALDI-TOF spectrum of G3.5(off). (b) SEC trace of G3.5(off). (c) SEC trace of G3.5(on).

It is well-known that anthracene derivatives undergo a [4+4] photocycloaddition upon irradiation. Thus, methanol solutions of the dendrons G1.5(off), G2.5(off), and G3.5(off) (ca. 0.12 M) were irradiated with a high-pressure mercury lamp ($\lambda > 300$ nm) at room temperature under a nitrogen atmosphere for 3 h to give dendrimers G1.5(on), G2.5(on), and G3.5(on) in 93, 74, and 83% yield, respectively (Scheme 2).[16] The structures of G1.5(on), G2.5(on), and G3.5(on) were confirmed by ^{1}H, ^{13}C NMR spectroscopies and elemental analyses.[17] The anthracene proton signals [δ 7.42 (t, 2H), 7.50 (t, 2H), 7.96 (d, 2H), 8.22 (d, 2H), 8.41 (s, 1H)] of G3.5(off) in $CDCl_3$ disappeared and new multiplet peaks appeared at 6.73–7.02 ppm which consist with formation of a dimer. A methylene proton signal [δ 5.39 (d, 2H)] of anthracene's 9-position of G3.5(off) disappeared and a new peak appeared at δ 4.51. Furthermore, the photocycloadducts were evidenced by the disappearance of UV absorption (300–400 nm) and the emergence of a new absorption (270 –290 nm) characteristic of an *o*-xylene system. This assignment is also supported by the appearance of a single peak corresponding to dendrimers G1.5(on), G2.5(on), and G3.5(on) in the SEC traces (Figure 1 (c)).

In order to clarify the utility of the anthracene moiety as photo-switch, we examined a retroreaction. On irradiation of methanol solutions of dendrimers G1.5(on), G2.5(on), and G3.5(on) (ca. 0.06 M) at 254 nm for 5 h, the original dendron G1.5(off), G2.5(off), and G3.5(off) were formed in 93, 94 and



Scheme 2. Structural control of poly(amide amine) dendrimer between G3.5(off) and G3.5(on).

100% yield, respectively.[16] Furthermore, dendrimers G1.5(on), G2.5(on), and G3.5(on) reverted back to the dendron G1.5(off), G2.5(off), and G3.5(off) on heating in the dark at 80 °C for 4 h in 97, 97, and 97% yield, respectively.[16]

Figure 2 shows time courses of the consumption of G1.5(off) and G3.5(off) in the photodimerization reactions and G1.5(on) and G3.5(on) in the retroreactions upon irradiation. Interestingly, despite increased steric hindrance for the higher generation, the addition and elimination efficiencies did not much depend upon the generation of dendrimers. It is notable that dendrons G1.5(off), G2.5(off), and G3.5(off) exhibit photochromic properties since fluorescence emission of anthracene is completely disappeared in anthracene dimer.

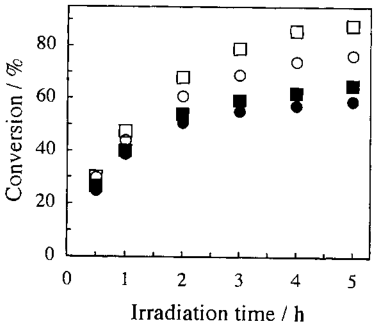


Figure 2. Time course of the consumption of G1.5(off) (□) and G3.5(off) (○) in the photodimerization reactions and G1.5(on) (■) and G3.5(on) (●) in the retro-reactions upon irradiation.

The results described herein show the first example of a controlling structure of a dendrimer having anthracene moiety at the core. The reversible switch between a dendron and a dendrimer is quite rare and an intermolecularly photoresponsive dendrimer has never been reported. Further work is in progress to explore the applications and advantages of the photoresponsive dendrimer having anthracene moiety.

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14 Selected data for G1.5(off): ^{1}H NMR ($CDCl_3$) δ 2.31 – 2.46 (m, 12H), 2.51–2.61 (m, 6H), 2.67–2.76 (m, 8H), 2.77–2.88 (m, 4H), 3.29–3.43 (m, 6H), 3.62 (s, 12H), 5.40 (d, *J* = 5.6 Hz, 2H), 6.87–7.00 (m, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.80 (t, *J* = 5.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.07 (t, *J* = 5.6 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 2H), 8.42 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 32.4, 33.0, 35.9, 36.90, 36.92, 49.0, 49.7, 51.5, 52.0, 52.7, 123.5, 125.1, 126.6, 127.1, 128.3, 129.1, 130.2, 131.3, 159.3, 159.6, 171.8, 172.9. for G2.5(off): ^{1}H NMR ($CDCl_3$) δ 2.35–2.43 (m, 24H), 2.49–2.54 (m, 12H), 2.58–2.63 (m, 6H), 2.70–2.75 (m, 16H), 2.78–2.84 (m, 12H), 3.23–3.30 (m, 8H), 3.32–3.39 (m, 6H), 3.65 (s, 24H), 5.44 (d, *J* = 5.6 Hz, 2H), 7.03–7.20 (m, 4H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.59–7.70 (m, 2H), 7.82–7.91 (m, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 8.19 (t, *J* = 5.6 Hz, 1H), 8.28 (t, *J* = 8.0 Hz, 2H), 8.46 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 32.2, 33.2, 33.5, 35.6, 36.7, 36.9, 48.8, 49.4, 49.5, 51.2, 51.69, 51.70, 52.0, 52.4, 123.3, 124.8, 126.3, 127.0, 127.9, 128.8, 129.9, 131.0, 159.1, 159.2, 171.9, 172.6, 173.0. for G3.5(off): ^{1}H NMR ($CDCl_3$) δ 2.23–2.38 (m, 64H), 2.41–2.59 (m, 30H), 2.61–2.80 (m, 56H), 3.14–3.31 (m, 30H), 3.58 (s, 48H), 5.39 (d, *J* = 5.6 Hz, 2H), 7.00–7.13 (m, 8H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.60–7.84 (m, 7H), 7.96 (d, *J* = 8.0 Hz, 2H), 8.16 (t, *J* = 5.6 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 2H), 8.41 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 29.3, 29.7, 32.6, 32.7, 33.8, 33.9, 36.0, 37.2, 37.5, 49.2, 49.8, 50.0, 50.7, 51.7, 52.1, 52.47, 52.53, 52.9, 123.8, 125.2, 126.8, 127.5, 128.4, 129.2, 130.4, 131.4, 159.6, 159.7, 172.4, 172.5, 172.8, 173.0.

15 As shown in Figure 1(a), there is a possibility of containing a little amount of defect structure of G3.5(off).

16 Product yield was defined as (isolated product weight (mg)) / (converted substrate weight (mg)) × 100.

17 Selected data for G1.5(on): ^{1}H NMR ($CDCl_3$) δ 2.23–2.48 (m, 24H), 2.50–2.66 (m, 12H), 2.69–2.95 (m, 24H), 3.14–3.47 (m, 12H), 3.69 (s, 24H), 3.89 (s, 2H), 4.50–4.74 (m, 4H), 6.77–6.96 (m. 16H), 7.22–8.03 (m, 10H). for G2.5(on): ^{1}H NMR ($CDCl_3$) δ 2.32–2.49 (m, 48H), 2.51–2.62 (m, 24H), 2.67–2.73 (m, 44H), 3.22–3.32 (m, 40H), 3.33–3.51 (m, 12H), 3.67 (s, 48H), 3.96 (s, 2H), 4.56 (brs, 4H), 6.77–7.08 (m, 18H), 7.12–7.61 (m, 12H), 8.07–8.52 (m, 4H). for G3.5(on): ^{1}H NMR ($CDCl_3$) δ 2.20–2.35 (m, 188H), 2.94–3.57 (m, 172H), 3.60 (s, 96H), 3.89 (brs, 2H), 4.49 (brs, 4H), 6.73–7.02 (m, 16H), 7.08–7.63 (m, 28H), 8.02– 8.52 (m, 4H).