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# Synthesis of novel dendrimers having a thermally reactive fluorescent core, and their thermal behavior

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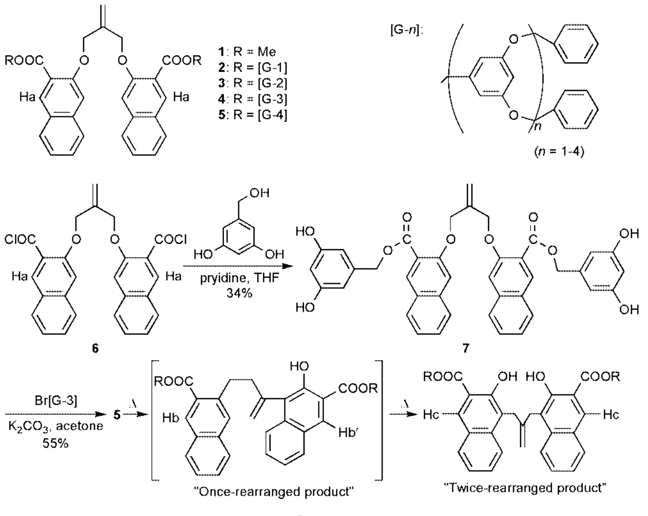
**Fluorescent poly(benzyl ether) dendrimers containing an isobutenyl and two naphthoate units at the core have been synthesized; thermal reaction (tandem Claisen rearrangement) of the dendrimers took place quantitatively, resulting in the complete quenching of the fluorescence.**

In recent years, dendrimers have been extensively employed for both basic and applied studies, principally owing to their well defined structures that enable functional groups to be accurately placed in dendrimer frameworks.[1] In particular, the light-harvesting function of dendrimers, one of the most unique and attractive dendritic effects, has recieved great attention in terms of biomimetic systems for photosynthesis.[2,3] Here we propose a fluorescent-controllable system using novel dendrimers with a reactive, fluorescent core that performs successive Claisen rearrangements.[4] Thermal Claisen rearrangement of high-generation dendrimers is expected to switch the emission property from ‘on’ to ‘off’ with a high contrast.

Dendrimers **2–4** were synthesized (Scheme 1) by a simple esterification of the corresponding dendritic wedges HO[G-*n*] with acid chloride **6** using triethylamine as base, and were isolated by preparative gel permeation chromatography (GPC), in moderate yields (18–69%). Polyether dendritic wedges HO[G-*n*] were obtained by following the convergent-growth method reported by Hawker and Fréchet.[5] However, esterification of the dendritic wedge HO[G-4] remarkably decreased the yield to 2.5% possibly due to the steric hindrance around the reactive site under these conditions. Hence, for the synthesis of the dendrimer **5**, we applied a divergent/convergent joint approach: **6** was first esterified with 3,5-dihydroxybenzylalcohol using pyridine to give **7** in 34% yield, followed by the etherification with a twice molar excess of the dendritic wedge Br[G-3] to obtain dendrimer **5** in 55% yield (Scheme 1). All dendrimers were characterized by $^1$H and $^{13}$C NMR, IR and MALDI-TOF mass spectra.†



**Scheme 1**

The absorption spectra of compounds **1–5** in CH$_2$Cl$_2$ are shown in Fig. 1, with spectral data summarized in Table 1. There are two clear absorption bands in all the spectra: one in the UV region (265–300 nm), due mainly to the dendritic wedges and the other in the near-UV region (305–385 nm), due only to the naphthyl moiety in the core. As the aromatic building unit of the dendritic wedges increases, the molar extinction coefficient ($\varepsilon$) at 280 nm increases almost proportionally, while the absorption at 345 nm remains unchanged, as expected, confirming the structure of the compounds (Scheme 1).

In order to investigate the light-harvesting effect of the dendrimers, steady-state emission spectra of the different generation dendrimers in CH$_2$Cl$_2$ were measured and the fluorescent quantum yields are summarized in Table 1. As the generation increases, there is a monotonic increase of the fluorescence intensity at 400 nm from the focal point upon excitation at 280 nm, where the dendritic wedges absorbed mostly in higher generation dendrimers. On the other hand, direct excitation of the naphthyl core at 345 nm gave a fluorescence at 400 nm without much difference in the quantum yields, 19–24% (Table 1). These results evidently demonstrate that this enhanced fluorescence is caused by an efficient energy transfer from the dendritic wedges to the naphthyl core in the higher generation dendrimer, in other words, the larger dendrimers serve as better antennae to collect photons, in accord with the report of Aida and coworkers on the light-harvesting effect of a poly(benzyl ether) dendron.[2] However, the energy transfer efficiency of the higher generation dendrimers **4** and **5**

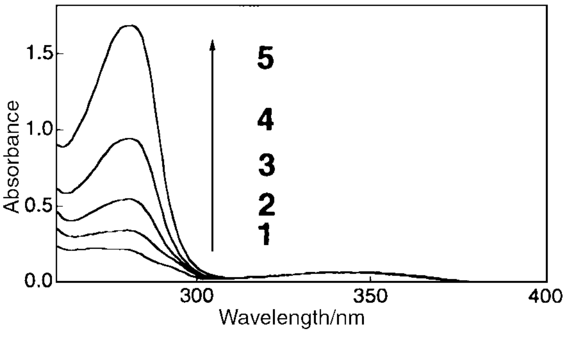


**Fig. 1** UV–VIS absorption spectra of dendrimers **1–5** in CH$_2$Cl$_2$. The spectra are normalized to 1.98 × 10$^{-5}$ M concentration.

**Table 1** Extinction coefficients at 280 and 345 nm, and fluorescent quantum yields around 400 nm upon excitation at 280 and 345 nm

| | 280 nm | | 345 nm | |
|---|---|---|---|---|
| Compound | $10^{-4}\ \varepsilon$/ M$^{-1}$ cm$^{-1}$ | $\Phi_{\mathrm{fl}}$ | $10^{-3}\ \varepsilon$/ M$^{-1}$ cm$^{-1}$ | $\Phi_{\mathrm{fl}}$ |
| **1** | 1.07 | 0.18 | 3.25 | 0.19 |
| **2** | 1.72 | 0.20 | 3.53 | 0.21 |
| **3** | 2.75 | 0.19 | 3.48 | 0.23 |
| **4** | 4.78 | 0.16 | 3.37 | 0.23 |
| **5** | 8.50 | 0.12 | 3.12 | 0.24 |

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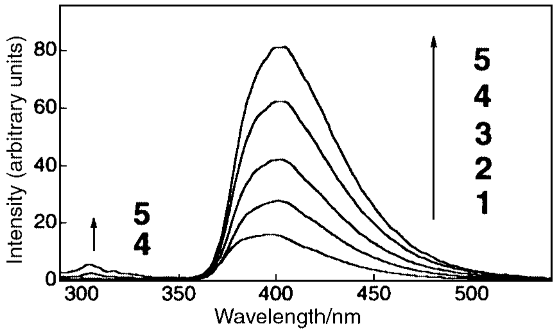

**Fig. 2** Steady-state fluorescence spectra of dendrimers **1**–**5** in $CH_2Cl_2$ upon excitation at 280 nm. The spectra are normalized to $0.99 \times 10^{-6}$ M concentration.

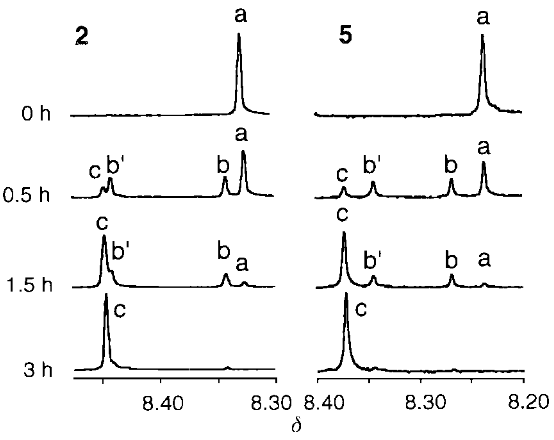

**Fig. 3** $^1$H NMR spectra of dendrimers **2** and **5** during the course of tandem Claisen rearrangement. Signals a, b, b′ and c arise from $H_a$, $H_b$, $H_{b'}$, and $H_c$ in the naphthoates (Scheme 1).

decreases somewhat, taking into account the fact that the residual fluorescence at 308 nm from the dendritic wedges was observed and even increased for **5**. There are some reports on the loss in energy transfer efficiency for higher generation dendrimers, probably due to many factors based on Förster's mechanism.[3,6] We believe that the relatively small spectral overlap between the fluorescence of the dendritic wedges and the absorption of the core might be one of the key factors to decrease the energy transfer efficiency, although more data is required to discuss this point fully. Another noteworthy finding is that there was no red-shifted emission due to the excimer, expected to be formed between the two neighboring chromophores, in any spectra of the dendrimers in $CH_2Cl_2$. By contrast, the model compound **1** in the solid state showed a broad excimer emission around 500 nm while no additional signal or peak shift appeared for **5**, which suggests that inter- rather than intramolecular interactions between the chromophores cause excimer formation; the dendritic wedge of **5** shields the focal point so effectively as to prevent intermolecular collision.

We compared tandem Claisen rearrangement of the core unit among the dendrimers to investigate the steric effect on the reaction. Almost quantitative tandem Claisen rearrangement of all the dendrimers took place over 3 h in the absence of solvent at 150 °C. Indeed the rearrangement occurred even at 105 °C though 3 days were required to complete the reaction. Fig. 3 shows $^1$H NMR spectra of dendrimers **2** and **5** during the course of tandem Claisen rearrangement at 150 °C. Surprisingly, there was no significant difference in the progress of the thermal reaction between the smaller and larger dendrimers. Indeed, the rate constants for this process were determined on the basis of the reasonable assumption that the rearrangement is a first-order successive reaction, to give almost identical rate-constants at 150 °C: $k_1 = 6 \times 10^{-4}\ s^{-1}$, $k_2 = 4 \times 10^{-4}\ s^{-1}$ for **2**; $k_1 = 6 \times 10^{-4}\ s^{-1}$, $k_2 = 5 \times 10^{-4}\ s^{-1}$, for **5**. These results show that even for the dendrimer with 32 benzyl groups at the periphery there is no steric hindrance and enough space to form a chair- or boat-like conformation, thought to be adopted for the [3,3] sigmatropic rearrangement.[7]

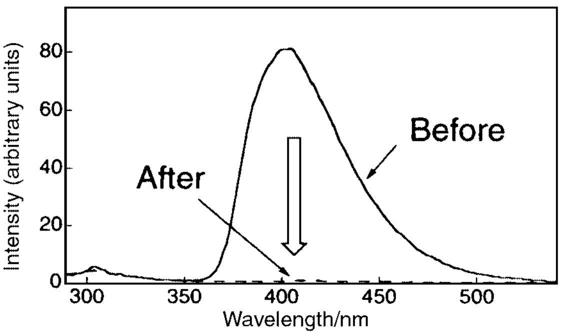

**Fig. 4** Steady-state fluorescence spectra of dendrimer **5** in $CH_2Cl_2$ upon excitation at 280 nm before and after tandem Claisen rearrangement. The spectra are normalized to $0.99 \times 10^{-6}$ M concentration.

Finally, the fluorescence spectra of the dendrimer **5** were compared before and after the rearrangement (Fig. 4). Interestingly, tandem Claisen rearrangement of the dendrimer resulted in complete quenching of the fluorescence around 400 nm with no change in the fluorescence at 308 nm arising from the dendritic wedge. We observed similar phenomena in the other dendrimers **1**–**4**. This indicates that the high generation dendrimers have potential to realize thermo- or photo-induced fluorescent images with high contrast.

In conclusion, we have demonstrated the light-harvesting effect of the fluorescent dendrimers having a reactive core for tandem Claisen rearrangement and their quenching by heating. Our finding that there is no steric hindrance on tandem Claisen rearrangement at the core of the dendrimers encourages us to incorporate other reactive groups into the core moiety such as carbamoyl, urea-type units in order to endow the dendrimer with new functions.

## Notes and references

† *Selected data: for* **2**: $\delta_H$ (500 MHz, $CDCl_3$): 4.81 (s, 4H), 4.96 (s, 8H), 5.28 (s, 4H), 5.49 (s, 2H), 6.54 (t, *J* 2.2 Hz, 2H), 6.68 (d *J* 2.2 Hz, 4H), 7.20 (s, 2H), 7.27–7.38 (m, 22H), 7.45 (t, *J* 8.1 Hz, 2H), 7.66 (d, *J* 8.1 Hz, 2H), 7.78 (d, *J* 8.1 Hz, 2H), 8.33 (s, 2H); MS (MALDI-TOF) m/z calc. for $C_{68}H_{56}O_{10}$ $[M + Na]^+$ 1056.2, found 1055.0. For **3**: $\delta_H$ (500 MHz, $CDCl_3$): 4.78 (s, 4H), 4.88 (s, 8H), 4.96 (s, 16H), 5.26 (s, 4H), 5.47 (s, 2H), 6.50 (t, *J* 2.3 Hz, 2H), 6.53 (t, *J* 2.3 Hz, 4H), 6.63 (d, *J* 2.3 Hz, 8H), 6.65 (d, *J* 2.3 Hz, 4H), 7.17 (s, 2H), 7.27–7.38 (m, 42H), 7.42 (m, 2H), 7.63 (d, *J* 8.3 Hz, 2H), 7.74 (d, *J* 8.0 Hz, 2H), 8.31 (s, 2H); MS (MALDI-TOF) *m*/*z* calc. for $C_{124}H_{104}O_{18}$ $[M + Na]^+$ 1905.1, found 1904.1. For **4**: $\delta_H$ (500 MHz, $CDCl_3$): 4.73 (s, 4H), 4.82 (s, 8H), 4.86 (s, 16H), 4.94 (s, 32H), 5.22 (s, 4H), 5.44 (s, 2H), 6.47–6.52 (m, 14H), 6.59–6.63 (m, 28H), 7.13 (s, 2H), 7.25–7.39 (m, 84H), 7.59 (d, *J* 8.1 Hz, 2H), 7.68 (d, *J* 8.1 Hz, 2H), 8.28 (s, 2H); MS (MALDI-TOF) *m*/*z* calc. for $C_{236}H_{200}O_{34}$ $[M + Na]^+$ 3603.1, found 3602.2. For **5**: $\delta_H$ (500 MHz, $CDCl_3$): 4.67 (s, 4H), 4.74 (s, 8H), 4.79 (s, 16H), 4.82 (s, 32H), 4.90 (s, 64H), 5.17 (s, 4H), 5.41 (s, 2H), 6.46–6.49 (m, 30H), 6.57–6.59 (m, 60H), 7.07 (s, 2H), 7.21–7.32 (m, 164H), 7.53 (d, *J* 8.1 Hz, 2H), 7.61 (d, *J* 8.1 Hz, 2H), 8.24 (s, 2H); MS (MALDI-TOF) *m*/*z* calc. for $C_{460}H_{392}O_{66}$ $[M + Na]^+$ 6999.0, found 6995.9.

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