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Synthesis and photoluminescence study of anthracene based dendrimer and dendron

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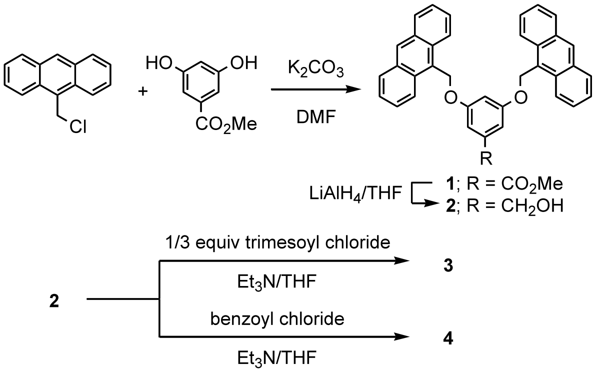
Abstract—A new type of polyaromatic dendrimer composed of six anthracene groups was synthesized, which showed a monomeric fluorescence feature with a diminished quantum yield due to intramolecular self-quenching processes in the dendritic framework. © 2003 Elsevier Science Ltd. All rights reserved.

Dendrimers, which have precisely hyper-branched architecture coupled with their spherical structures, have attracted great deal of interests due to remarkable availability for applications in many fields.[1–3] A lot of elaborations have therefore been paid for syntheses of new dendrimers in order to create intriguing functionalities such as photo-harvesting antenna effect of aromatic dendrimers.[4–7] In this regard, rational design of dendritic frameworks permits many variations in the number and arrangement of molecular components through covalent or noncovalent bondings.[8,9] Multiple accumulation of π-electron enriched aromatic components in well-ordered array of dendritic frameworks may yield close packing of functional groups, which allows effective π-stacked arrangement and extended aromatic π-systems suitable for a fabrication of efficient electronic and photochemical devices.[10–13] An interesting alternative for the synthesis of the polyaromatic dendrimers is modification of aromatic groups. Based on this consideration, anthracene was applied to a component of dendritic architecture because this molecule has been recognized as an attractive material in its photochemical and electrochemical properties as well as used as a potential medium for photoconductive and electroluminescence devices.[14–17] In this communication, we disclose a primitive type of anthracene-based dendrimer bearing six anthracene units, which showed integrated absorption and fluorescence properties characteristic of monomeric anthracenes. In the course of an investigation of the photoluminescence study, we discovered that dendritic framework facilitated intramolecular energy migration from branch to branch resulting in a lower fluorescence quantum yield.

The synthesis of branched structure utilized ether linkages to couple 2 equiv. of anthrylmethyl chloride and methyl 3,5-dihydroxybenzoate (Scheme 1). The reaction proceeded efficiently with heating the mixture in the presence of potassium carbonate in DMF solution at 70°C for 3 h, affording methyl 3,5-bis(anthrylmethoxy)benzoate **1** in 93% yield. The ester group of **1** was subsequently converted to alcohol by treatment with lithium aluminum hydride in anhydrous THF solution giving the corresponding alcohol **2** quantitatively (96%). Finally, condensation of 3 equiv. of **2** and



Scheme 1. Synthetic routes to dendrimer **3** and dendron **4**.

Keywords: anthracene; dendrimer; fluorescence; microcrystals; excimer; intramolecular energy migration.

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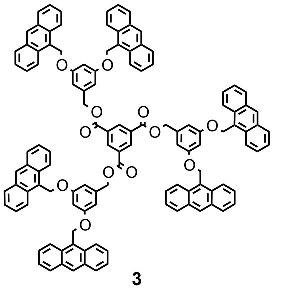
trimesoyl chloride gave rise to the target dendrimer **3** in 75% yield. Additionally, benzoyl-capped dendron **4** was quantitatively synthesized as a structurally simplified analogue of **3** (98%).



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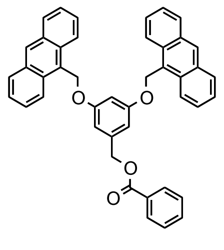

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These compounds were well characterized by spectroscopic data[18] while the structure of **4** was unequivocally established by X-ray crystallography.[19] The fast atom bombardment (FAB) mass spectra gave clear evidence for the structures with mass ion peaks at *m*/*z* 1718 (MH^+) for **3** and *m*/*z* 624 (M^+) for **4**, respectively. Inspection of the ^1H and ^{13}C NMR spectra clearly reveals that **3** is highly symmetric in structure to provide sufficient information on the structural assignment with distinct signals. Figure 1 shows the ^1H NMR spectrum of **3**, where a singlet absorption at 8.99 ppm is attributed to the benzoyl protons located at the focal point of the dendritic structure. The multiple resonances from 7.3 to 8.5 ppm fit into a typical pattern of the 9-substituted anthryl group while aromatic protons of the resorcinol moieties appear at 6.88 ppm. The resonances assignable to the methylene protons adjacent to the anthryl and phenyl groups occurred at 5.87 and 5.40 ppm, respectively, providing a pair of singlets.

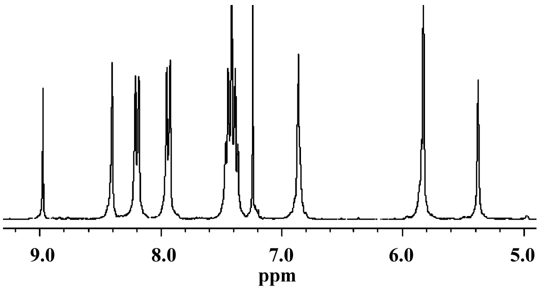

Figure 1. ^1H NMR spectrum of dendrimer **3**.

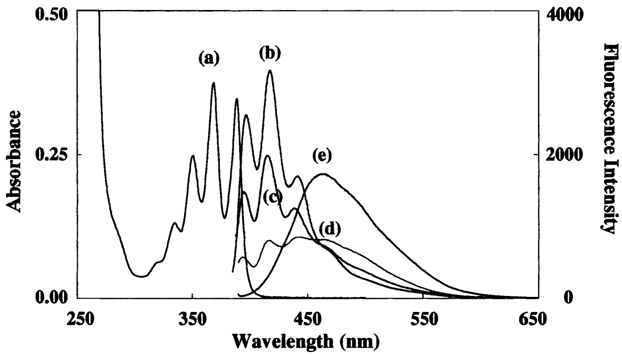

Figure 2. Absorption and fluorescence ($\lambda_{ex}=380$ nm) spectra of dendrimer **3**: (a) absorption spectrum of **3** in $CHCl_3$; (b)–(e) fluorescence spectra of **3** in $CHCl_3$–hexane mixture in ratios of; (b) 100:0, (c) 33:67, (d) 25:75, (e) 3:97. The concentrations of **3** in $CHCl_3$ or $CHCl_3$–hexane mixture were 10.9 μmol/L for all samples.

In an effort to gain further insights into the electronic states of the molecular system, its spectroscopic property was elucidated by absorption and fluorescence observations. Figure 2 summarizes the spectroscopic profiles of **3**. In analogy to anthracene,[20] the absorption spectrum of **3** in chloroform showed a typical pattern due to the anthracene chromophores in the 350–400 nm region with the integrated absorption coefficients while excitation of the solution at 380 nm resulted in an intense fluorescence peak centered at 420 nm. However, changes in solvent polarity used for the observation from chloroform to hexane caused degradation of the fluorescence intensity with proportional growth of a shoulder at 470 nm in the photoluminescence spectrum accompanied by deposition of insoluble microcrystals in the solution. Ultimately, a distinct peak assignable to an excimer emission was obtained by fluorescence observation of the suspended hexane solution. Such an effect on the emission shift can be interpreted in terms of solute–solute interactions involving aromatic π–π stacking of ground-state anthracenes, which facilitate incidental excimer formation along with fluorescence quenching in a nonradiative pathway. However, removal of the deposited material from the coagulated solution by filtration revealed that the dendrimer solubilized in hexane exhibited the monomeric fluorescence with complete loss of the excimer peak in the spectrum. This observation suggests that the excimer fluorescence should be derived from effective overlaps of the anthracenes in the microcrystalline sites.[21] With regard to detailed structural description of **3**, structure of the corresponding dendron **4**, which exhibited similar trends in the fluorescence spectra with both solvents employed (Fig. 3),[22] was confirmed by X-ray crystallographic analysis. According to the X-ray structure as depicted in Figure 4, the anthracene substituents would

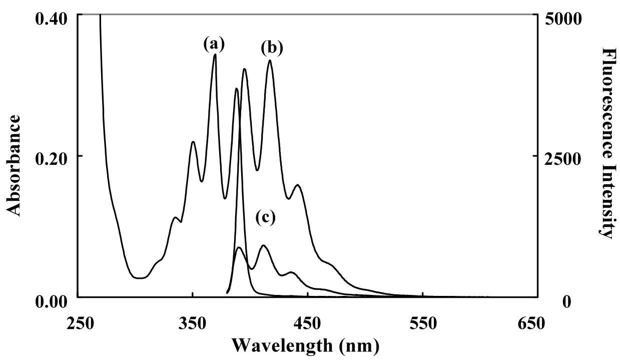

Figure 3. Absorption and fluorescence spectra of dendron **4**: (a) absorption spectrum of **4** in $CHCl_3$ (*c* 22.0 μmol/L); (b) fluorescence spectra of **4** in $CHCl_3$ (*c* 5.5 μmol/L, $\lambda_{ex}=370$ nm); (c) fluorescence spectra of **4** in hexane (*c* 5.5 μmol/L, $\lambda_{ex}=365$ nm).

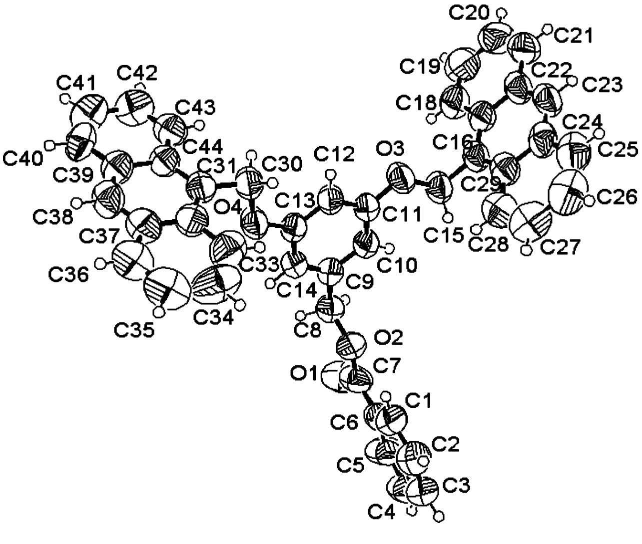

Figure 4. ORTEP drawing of dendron **4**.

be preferentially oriented away from another, where the π–π orbital interaction required for intramolecular excimer formation should be avoided. In such a case, the molecules in solution may adopt a similar conformation unfavorable for the intramolecular excimer formation as in the crystalline state.[23] The above rationalization based on the conformational restrictions can account for the failure of the intramolecular excimer formation of **4**. Likewise, such a conformational criterion can be applied to the dendritic system where the neighboring anthracenes should be sufficiently separated each other. On the basis of the above consideration, it is concluded that the dendritic framework offers an intrinsically dispersed packing arrangement of the anthracene components, which displayed intense fluorescence due to the monomeric species of anthracenes.

In addition, an attempt was made to determine fluorescence quantum yields of **3** and **4** by referring to the value of anthracene as a standard.[20] Table 1 shows an impressive difference in the fluorescence yields between two dendritic analogues, where the quantum efficiency of **3** was almost 60% lower than that of **4**. Considering the lack of intramolecular excimer formation in this dendritic system, the difference in quantum yields was most likely due to a consequence of self-quenching by nonradiative pathways between closely located chromophoric groups.[24] In this regard, a dilution study of **3** was carried out in order to accommodate a mechanistic interpretation. This revealed that chloroform solutions of **3** at different concentrations exhibited linearity of fluorescence intensities with concentrations employed in a range from 10^{-7} to 10^{-5} M. This observation suggests that intramolecular fluorescence quenching should be coherent in this molecular system. Therefore, we can conclude that the intramolecular energy migration from branch to branch is an intrinsic feature of this dendritic framework.

Table 1. Absorption and fluorescence emission data for the determination of fluorescence quantum yields (Φ_F) of **3** and **4**

Entry	λ_{ex} (ε (cm^{-1} M^{-1}))	λ_{em} (nm)	Φ_F
Anthracene[a,b]	365 nm (2,900)	380, 402, 425, 452	0.27
3[c]	377 nm (18,000)	398, 418, 443, 472[d]	0.13
4[c]	377 nm (6,500)	396, 418, 442, 472[d]	0.32

[a] Ref. 20.

[b] Measured in ethanol (*c* 5.5 μmol/L).

[c] Measured in $CHCl_3$ (*c* 5.5 μmol/L).

[d] Observed as shoulder peaks.

In conclusion, a new type of polyaromatic dendrimer composed of six anthracene groups was synthesized using a convergent strategy. In a diverse and densely arrayed supramolecular system, anthracene groups exhibited monomeric fluorescence with a diminished quantum yield in solution media due to intramolecular self-quenching processes. This observation demonstrates that the present dendritic system allows significant interactions between divergently disposed chromophores, indicating a possibility of potential applications to artificial light-harvesting and light-emitting supramolecular devices such as a fluorescence resonance energy transfer (FRET) system.[25,26] Further synthetic elaboration of structural modifications focusing on functionalization of the surface groups, development of higher generation dendrimers, and incorporation of functional molecules at the focal point is now in progress.

Acknowledgements

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18. Spectral data: **1**; mp 250–251°C; IR (KBr) 1716 cm^{-1} (C=O); LRMS (FAB) m/z 548 (M^+, calcd for $C_{38}H_{28}O_4$: 548.2); ^1H NMR ($CDCl_3$) δ 3.94 (s, 3H, *Me*), 5.99 (s, 4H, CH_2), 7.07 (t, $J=2.2$ Hz, 1H, Ar*H*), 7.4–7.6 (m, 10H, Ar*H*), 8.04 (d, $J=8.1$ Hz, 4H, Ar*H*), 8.27 (d, $J=8.6$ Hz, 4H, Ar*H*), 8.53 (s, 2H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 52.3, 63.2, 107.3, 108.7, 123.9, 125.1, 126.7, 129.1, 129.2, 129.3, 131.1, 131.5, 139.0, 160.4, 166.9. **2**; mp 198–199°C; IR (KBr) 3735 cm^{-1} (OH); LRMS (FAB) m/z 520 (M^+, calcd for $C_{37}H_{28}O_3$: 520.2), 543 (MNa$^+$, calcd for $C_{37}H_{28}O_3Na$: 543.2); ^1H NMR ($CDCl_3$) δ 1.72 (t, $J=5.7$ Hz, 1H, O*H*), 4.75 (d, $J=5.7$ Hz, 2H, CH_2), 5.97 (s, 4H, CH_2), 6.89 (s, 3H, Ar*H*), 7.4–7.6 (m, 8H, Ar*H*), 8.04 (d, $J=7.9$ Hz, 4H, Ar*H*), 8.29 (d, $J=8.4$ Hz, 4H, Ar*H*), 8.53 (s, 2H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 62.9, 65.4, 101.2, 106.1, 124.0, 125.1, 126.6, 129.0, 129.1, 129.3, 131.1, 131.5, 143.7, 160.7. **3**; mp 193–194°C; UV ($CHCl_3$) 351 nm (ε 30800), 369 nm (ε 46500), 388 nm (ε 42800); IR (KBr) 1727 cm^{-1} (C=O); LRMS (FAB) m/z 1718 (MH$^+$, calcd for $C_{120}H_{85}O_{12}$: 1716.6); ^1H NMR ($CDCl_3$) δ 5.40 (s, 6H, CH_2), 5.87 (s, 12H, CH_2), 6.88 (s, 9H, Ar*H*), 7.3–7.6 (m, 24H, Ar*H*), 7.96 (d, $J=8.3$ Hz, 12H, Ar*H*), 8.22 (d, $J=8.1$ Hz, 12H, Ar*H*), 8.43 (s, 6H, Ar*H*), 8.99 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 62.9, 67.3, 102.0, 107.6, 125.0, 126.5, 126.6, 129.1, 131.0, 131.4, 135.1, 138.1, 138.4, 160.7, 164.8. Anal. calcd for $C_{120}H_{84}O_{12}$: C, 83.90; H, 4.93; N, 0.00. Found: C, 83.95; H, 4.86; N, 0.03. **4**; mp 202–203°C; UV ($CHCl_3$) 351 nm (ε 10000), 370 nm (ε 15600), 388 nm (ε 13400); IR (KBr) 1710 cm^{-1} (C=O); LRMS (FAB) m/z 624 (M^+, calcd for $C_{44}H_{32}O_4$: 624.2), 663 (MK$^+$, calcd for $C_{44}H_{32}O_4K$: 663.2); ^1H NMR ($CDCl_3$) δ 5.38 (s, 2H, CH_2), 5.86 (s, 4H, CH_2), 6.89 (s, 3H, Ar*H*), 7.3–7.6 (m, 11H, Ar*H*), 7.98 (d, $J=8.1$ Hz, 4H, Ar*H*), 8.07–8.10 (m, 2H, Bz*H*), 8.24 (d, $J=8.6$ Hz, 4H, Ar*H*), 8.46 (s, 2H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 62.8, 66.5, 101.4, 107.2, 123.9, 125.0, 126.5, 126.6, 128.4, 129.1, 129.7, 130.0, 131.0, 131.4, 133.0, 138.7, 160.7, 166.4. Anal. calcd for $C_{44}H_{32}O_4$: C, 84.59; H, 5.16; N, 0.00. Found: C, 84.59; H, 5.07; N, 0.02.
19. Crystal data for **4**: $C_{44}H_{32}O_4$, $M=624.7$, triclinic space group $P\bar{1}$ (#2), $D_{calcd}=1.27$ g cm^{-3}, $Z=2$, $a=12.5637(18)$ Å, $b=12.9072(15)$ Å, $c=11.5164(17)$ Å, $\alpha=98.307$ (12)°, $\beta=117.232$ (11)°, $\gamma=82.657$ (11)°, $V=1639.1$ (4) Å^3. All independent 4871 reflections were collected with 434 variables. Final R_1 $(F)=0.0585$ for 3040 reflections, R_1 $(F)=0.0978$ for all data, and wR_2 $(F^2)=0.1173$ for all data. The Crystallographic Information File (CIF) including atomic coordinates, bond lengths and angles, and thermal parameters was deposited at the Cambridge Crystallographic Data Center.
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23. The molecular modeling of **4** obtained by molecular dynamics simulations suggested that significant conformational distortions around the benzene ring of the branching point prevented effective overlap of the anthracene rings, although the anthracene substituents were mobile within the flexible structure.
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