Synthesis and fluorescence properties of dansyl labeled triazine dendrons

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Abstract. A series of fluorescent dendrons with dansulfonyl group as a fluorophore attached at the focal point were synthesized by a convergent method. There was no need for tedious and lengthy protection/deprotection or chromatographic separation. The method provided simple operation and high yield. Their fluorescence characteristic in dichloromethane was investigated. The results indicated that the dendritic modification had positive effect on the emission of fluorescence, and the emission maximum of dansylated dendrons was enhanced up to 20-fold. Meanwhile, the fluorescent intensity of dansylated dendrons could be remarkably improved with the increase of dendron generation. These findings can contribute significantly to the general understanding of the dendron systems and also for potential applications in photochemical molecular devices and organic electroluminescent devices.

1. Introduction
Dendrimers are a class of macromolecules with the characteristics of regular branches, high symmetry, and rigidity, which exhibit special properties such as good solubility and flexibility [1, 2]. Nowadays, dendrimers have long been attracting attention and extensively studied because of their possible applications in many fields, such as catalysis, drug-delivery, MRI contrast agents [3, 4].

Dendrimer functionalization contributes new properties and applications. The functionalization of dendritic structures with chromospheres enables them to be photoactive with potential applications in photochemical molecular devices. These compounds have also been investigated for use as electroluminescent devices [5, 6]. Recently, many dendrimers with fluorophore core have been synthesized. After dendritic modification, their fluorescent properties have been greatly altered. Fluorescence spectroscopy has been used to study the effect of dendritic shielding on the core of the molecule [7, 8].

In particular dansylated dendrons have engrossed much attention due to their excellent luminescent properties [9-13]. In order to gain a better understanding of the microenvironment of the dendrons created at the core and the effect of the dendron branching on the core, we provide an extensive photophysical idea about the second generation of triazine dendrons with ethyl end groups and dansyl moiety. Compared with the small dansulfonyl group that has weak fluorescence, the triazine dansylated dendrons have remarkable fluorescence properties.
2. Experimental

2.1. Materials and instruments
All chemicals, reagents, and solvents were used as received from commercial sources without further purification. Dichloromethane was refluxed and distilled with CaH₂. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker spectrometer. The FTIR spectra were recorded via the KBr pellet method by using a Nicolet iS10 FTIR spectrophotometer. The photoluminescence were recorded on a Hitachi F-4500 spectrofluorimeter. Excitation and emission slits were set at 5/5 nm.

2.2. Dendrimer synthesis
The synthetic route to the triazine dansylated dendrons is illustrated in Figure 1.

Figure 1. Synthetic route of triazine dansylated dendrons.
Reagents and conditions: (a) DEA, DIPEA, 0 °C, 2 h; (b) piperazine, reflux, 18 h; (c) cyanuric chloride, DIPEA, 0 °C, 24 h; (d) CH3CN, K2CO3, 0 °C, 18 h

**Synthesis of compound 1.** Diethylamine (0.70 g, 9.52 mmol) and diisopropylethylamine DIPEA (1.56 mL, 9.52 mmol) were added into 80 mL dichloromethane and cooled in salt/ice-bath, then add cyanuric chloride (0.80 g, 4.33 mmol) into the solution. The resulting mixture was stirred in ice-bath for 0.5 h and then at room temperature for 8 h. The reaction mixture was washed with 5 mol/L diluted HCl (2 × 50 mL), then distilled water (2 × 100 mL), and dried by sodium sulfate. The solvent was removed at reduced pressure and dried in a vacuum oven at 60°C until constant weight was maintained, then 1.18 g (96.5%) of product 1 as a yellow liquid is obtained.

1H NMR (400 MHz, CDCl3) δ 1.08 (t, 12H, J = 7 Hz), 3.47 (q, 8H, J = 7 Hz). 13C NMR (100 MHz, CDCl3) δ 12.8, 13.4, 41.4, 41.6, 164.0, 168.7. IR (KBr) ν 2976, 2934, 1568, 1551, 1492 cm⁻¹.

**Synthesis of compound 2.** Intermediate 1 (1.06 g, 4.11 mmol) was dissolved in THF (50 mL) then add piperazine (1.80 g, 20.61 mmol). The solution was stirred for 24 h and then evaporated under vacuum. The residue was dissolved in dichloromethane, washed with KOH (1.20 g, 20.56 mmol) in water (100 mL), then water (2 × 50 mL) and dried by anhydrous sodium sulfate. 1.21 g (99.9%) of product 2 was obtained as a yellow liquid.

1H NMR (400 MHz, CDCl3) δ 1.02 (t, 12H, J = 7 Hz), 2.75 (t, 4H, J = 5 Hz), 3.30 (s, 1H), 3.42 (q, 8H, J = 7 Hz), 3.63 (t, 4H, J = 5 Hz). 13C NMR (100 MHz, CDCl3) δ 13.3, 41.1, 44.1, 45.9, 164.7, 165.5. IR (KBr) ν 3310, 3298, 2971, 2930, 2849, 1580, 1516, 1466, 1366, 1275, 1149, 1082, 982 cm⁻¹.

**Synthesis of compound 3.** Intermediate 2 was dissolved in dichloromethane (50 mL) was cooled in salt/ice-bath before cyanuric chloride (0.31 g, 1.69 mmol) was added. The reaction solution was stirred in ice-bath for an hour. The reaction solution was washed with 5 mol/L diluted HCl (2 × 50 mL), then water (2 × 50 mL) and dried over sodium sulfate. Product 3 1.66 g (93.5%) was obtained as a white solid.

1H NMR (400 MHz, CDCl3) δ 1.16 (t, 24 H, J = 7 Hz), 2.36 (q, 16H, J = 6.9 Hz), 2.62 (s, 1H), 2.88 (t, 4H, J = 4.5 Hz), 3.56 (q, 24H, J = 6.9 Hz), 3.76-3.78 (m, 20H). 13C NMR (100 MHz, CDCl3) δ 13.5, 41.1, 43.1, 43.2, 44.3, 46.1, 164.7, 165.4, 165.4, 165.6. IR (KBr) ν 3332, 3298, 2971, 2929, 2849, 1580, 1516, 1466, 1366, 781 cm⁻¹.

**Synthesis of compound 4.** Intermediate 3 (1.66 g, 1.58 mmol) was dissolved in THF (50 mL) and piperaocine (410 mg, 4.76 mmol) was added. The solution was stirred at reflux for 24 h and then evaporated under vacuum. The residue was dissolved in dichloromethane, washed with KOH (0.45 g, 8.01 mmol) in water (100 mL), then dried by anhydrous sodium sulfate. Solvent was removed at reduced pressure to afford 1.16 g (95.1%) of product 4 as a yellow liquid.

1H NMR (400 MHz, CDCl3) δ 1.14 (t, 24 H, J = 6.9 Hz), 2.26 (s, 1H), 2.88 (t, 4H, J = 4.5 Hz), 3.56 (q, 24H, J = 6.9 Hz), 3.76-3.78 (m, 20H). 13C NMR (100 MHz, CDCl3) δ 13.5, 41.1, 43.1, 43.2, 44.3, 46.1, 164.7, 165.4, 165.4, 165.6. IR (KBr) ν 3332, 3298, 2971, 2929, 2849, 1580, 1516, 1466, 1366, 781 cm⁻¹.

**Synthesis of compound 5.** Intermediate 2 (100 mg, 0.325 mmol) and K2CO3 (49.4 mg, 0.39 mmol) were dissolved in CH2CN (100 mL), dansyl chloride (DNSCl) (88 mg, 0.325 mmol) is added to the solution. The resulting mixture was stirred in ice-bath for an hour and the reaction mixture was allowed to cool to room temperature. The reaction mixture was washed with distilled water (3 × 100 mL), and dried by anhydrous sodium sulfate. The solvent was removed at reduced pressure and dried in a vacuum oven at 100 °C until constant weight was maintained, giving crude product 5 as a green yellow solid (171 mg, 97.4%).

1H NMR (400 MHz, CDCl3) δ 1.08 (t, 12H, J = 6.9 Hz), 2.88 (s, 6H), 3.18 (t, 4H, J = 4.6 Hz), 3.47(q, 16H, J =6.9 Hz), 3.80(t, 4H, J = 5.6 Hz), 7.18(d, J = 7.5 Hz, 1H), 7.54(t, J = 7.6 Hz, 2H), 8.20(d, J = 7.2 Hz, 1H), 8.46(d, J = 8.6 Hz, 1H), 8.56 (d, J = 8.6 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 11.5, 11.5, 39.1, 40.7, 43.5, 43.7, 113.3, 114.6, 117.8, 121.3, 126.1, 128.2, 128.6, 128.7, 128.8, 130.6, 149.8, 162.6, 163.2. IR (KBr) ν 3079, 2972, 2930, 2864, 1648, 1612, 1534, 1499, 1432, 1326, 1275, 793 cm⁻¹.

**Synthesis of compound 6.** Intermediate 4 (0.252 g, 0.325 mmol) and K2CO3 (0.049 g, 0.36 mmol) were dissolved in CH2CN (100 mL), and cooled in salt/ice-bath, dansyl chloride (88 mg, 0.325 mmol)
was added to the solution. The resulting mixture is stirred in ice-bath for 1 h. The reaction mixture was washed with distilled water (3 × 100 mL), and dried by anhydrous sodium sulfate. The solvent was removed at reduced pressure and dried in a vacuum oven at 100 °C until constant weight was maintained, then the product 6 (309 mg, 94.3%) as a yellow green solid is obtained.

\[^1H\text{NMR} (400 \text{ MHz, CDCl}_3) \delta 1.13 (q, 24H, J = 6.9 \text{ Hz}), 2.89 (s, 6H), 3.17 (t, 4H, J = 4.6 \text{ Hz}), 3.53 (q, 16H, J = 6.9 \text{ Hz}), 3.79 (t, 16H, J = 6.9 \text{ Hz}), 3.81 (t, 8H, J = 6.9 \text{ Hz}), 7.17 (d, 1H, J = 7.5 \text{ Hz}), 7.53 (t, 2H, J = 7.2 \text{ Hz}), 8.19 (d, 1H, J = 8.6 \text{ Hz}), 8.48 (d, 1H, J = 8.6 \text{ Hz}), 8.55 (d, 1H, J = 8.6 \text{ Hz}). \]^13C\text{NMR} (100 \text{ MHz, CDCl}_3) \delta 13.5, 41.1, 42.7, 43.0, 43.1, 45.4, 45.7, 53.4, 115.3, 119.8, 123.2, 128.1, 130.1, 130.6, 130.7, 132.6, 151.8, 164.8, 165.1, 165.3, 165.6. \text{IR (KBr)} \nu 3080, 2973, 2930, 2859, 1612, 1533, 1484, 1432, 1325, 1266, 735 \text{ cm}^{-1}.

3. Results and discussion

3.1. The solubility of dansylated dendrons in different solvents

Compound 5 and compound 6 (10 mg) are added to 1 mL solvents, and stirred for 10 mins. The solubility in some general solvents is tested, as show in Table 1. The experimental results indicate that compound 5 and compound 6 have good solubility in these solvents, such as CH\textsubscript{2}Cl\textsubscript{2}, THF, CH\textsubscript{3}CN, DMF. But they are not insoluble in strong polar solvents such as CH\textsubscript{3}OH and H\textsubscript{2}O.

Table 1. The solubility of triazine dansylated dendrons.

| Compound | CH\textsubscript{2}Cl\textsubscript{2} | EtOAc | THF | CH\textsubscript{3}CN | DMF | CH\textsubscript{3}OH | H\textsubscript{2}O |
|----------|-----------------|---------|-----|-----------------|-----|----------------|---------|
| DNSCl    | dissolved       | dissolved| dissolved | dissolved | dissolved | undissolved | undissolved |
| Compound 5 | dissolved       | dissolved| dissolved | dissolved | dissolved | undissolved | undissolved |
| Compound 6 | dissolved       | dissolved| dissolved | dissolved | dissolved | undissolved | undissolved |

3.2. Fluorescence emission properties

**Fluorescence studies.** As shown in Figure 2, the fluorescent spectra of compound 5 and compound 6 in dichloromethane at room temperature. Without dendritic modification, the fluorescent emissions of DNSCl is observed at 443 nm, and it has very weak fluorescence upon excitation at 360 nm. When dansulfonyl group is modified by dendritic structures, due to the intramolecular charge transfer effect, the compound 5 and compound 6 both show remarkably strong fluorescence under the same conditions. Exit at 360 nm, both of the emission maximum of compound 5 and compound 6 are observed at 500 nm. For different generations of dansylated dendrons, the absorption spectral maxima keep stable. This phenomenon indicates that the essential charge transfer character of the transition remains similar for compound 5 and compound 6.

Compared with single DNSCl, introduction of dendritic part into dansulfonyl core has positive effect on the emission of fluorescence, and the emission maximum of dansylated dendrons is enhanced up to 20-fold. The evident shows that the fluorescence intensity could be strengthened remarkably as the generation increased. The fluorescent intensity of dansylated dendrons could be remarkably improved with the increasing generation. This phenomenon may be explained as follows: the mutual isolation between different dansulfonyl cores could be achieved by the position isolation of dendritic shell and the shield effect of dendrons. As a result, the fluorescence concentration quenching between different dansulfonyl cores could be reduced.
Figure 2. Fluorescence spectra of DNSCl, compound 5 and compound 6 in CH$_2$Cl$_2$ (1.0 × 10$^{-5}$ mol/L) at room temperature (360 nm).

Concentration effect studies. The concentration effect on the fluorescent emission of compound 6 is investigated in CH$_2$Cl$_2$ solution at room temperature (Figure 3). When the concentration of compound 6 ranges from 1 × 10$^{-3}$ mol/L to 1 × 10$^{-5}$ mol/L, there is a blue shift in absorption, and the relative intensity increases. However, change of the concentration from 1 × 10$^{-5}$ mol/L to 1 × 10$^{-6}$ mol/L causes the relative fluorescence intensity to reduce significantly. The intensity at the concentration of 1 × 10$^{-3}$ mol/L is even lower. The compound 6 (1 × 10$^{-5}$ mol/L) has the maximum relative fluorescence intensity. Quite low intensity results from the molecular aggregation and fluorescence quenching.

Figure 3. Concentration effect on the fluorescent emission of compound 6 at room temperature.
4. Conclusions

1) Two generations of triazine dendrons with ethyl end group having a dansyl moiety attached at the focal point have been presented by the divergent synthesis.

2) The triazine dansylated dendrons are could be efficiently synthesized without employing protection/deprotection or chromatographic separation steps. Moreover, these compounds have good solubility in common organic solvents.

3) The triazine dansylated dendrons have strong fluorescence features compared with the corresponding small dansulfonyl group. The results of this study are significative to design efficient photochemical molecular devices and organic electroluminescent devices.

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