

Convergent Syntheses of Dendrimers Having Photo-responsive and Redox-active Unit

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Dendrimers are well-defined, tree-like macromolecules, with a high degree of order and the possibility to contain selected chemical units in predetermined sites of their structure. Dendrimers are currently attracting the interest of many scientists because of their unusual chemical and physical properties and the wide range of potential applications. It is possible to design and synthesize dendrimers containing a variety of functional groups that can be useful for various field and purposes.¹ Dendrimers have great potential as such nano-scale molecules.

During the past two decades various dendrimers with different cores, branches, and end groups have been synthesized and applied in different area including drug-delivery, catalysis, light energy harvesting, sensor, etc.² Dendrimers with photo and/or redox-active components have been proposed as promising materials for miniaturized information storage.³⁻¹⁰ Therefore syntheses of nano-scale molecules possessing device-like properties are of much interest in modern science and technology. In conjunction with our program directed at the design and syntheses of nano-structured functional materials, we herein present the high yielding and first synthesis of dendrimers which contain a *trans*-1,2-bis(4-pyridyl)ethylene residue with two

identical Fréchet-type dendrons (first to third generation).

The synthetic strategy for the preparation of dendrimers utilized a convergent method (Figure 1).^{2d} The most attractive feature of the convergent synthesis is that requires a very small number of transformations per molecule in the coupling step. The reaction can be driven to completion with equivalent or only a slight excess of reagent, providing greater structural control in preparing well-defined unsymmetrical dendrimers. Prior to the synthesis of dendrimers, the benzyl bromide dendrons **1-Dm** ($m = 1, 2,$ and 3 : generation of dendron) were prepared according to the reported procedure.¹¹ To probe the viability of our approach, the coupling was initially studied using low generation dendron bromide in various solvents such as THF, CH₃CN, DMF, and DMSO. We were pleased to find that the reaction between *trans*-1,2-bis(4-pyridyl)ethylene **2** and three molar equivalents of dendron bromide **1-D1** in DMSO for 48h at room temperature afforded the symmetrical dendrimer **3-G1** in 98% yield. With this result, we next examined the reaction with higher generation dendron bromides. Reaction between *trans*-1,2-bis(4-pyridyl)ethylene **2** and three molar equivalents of the corresponding dendron bromides **1-Dm** in DMSO for 48h at room temperature afforded the symmetrical dendrimers **3-Gm** with redox active and photo-responsive unit in 95% and 86% yields for **G2** and **G3**, respectively.

The purification of the resulting compounds was achieved by precipitation adding non-polar solvent such as THF, EtOAc, and diethyl ether, because these dendrimers have two positive charges. Eventually we can prepare highly pure dendrimers by a convergent method. The yield of dendrimers (**3-G1** and **3-G2**) with low generation dendrons is higher than those (**3-G3**) with high generation dendron. The somewhat lower isolation yield of the latter may be due to their higher solubilities in non-polar solvent used to remove excess dendron components. The structures of all compounds were confirmed by ¹H and ¹³C NMR spectroscopy and they were exhibited very good correlation with the calculated molecular masses as evidenced by their FAB and/or MALDI-TOF mass spectra.¹²

The symmetrical dendrimers **3-Gm** contain two types of chromophoric units, namely 1,2-bispyridinium ethylene and 1,3-dialkoxybenzene. The ratios of these two types of units are 1 : 2 for **3-G1**, 1 : 6 for **3-G2** and 1 : 14 for **3-G3**. The absorption spectra of **3-G1** and **3-G3** in acetonitrile-

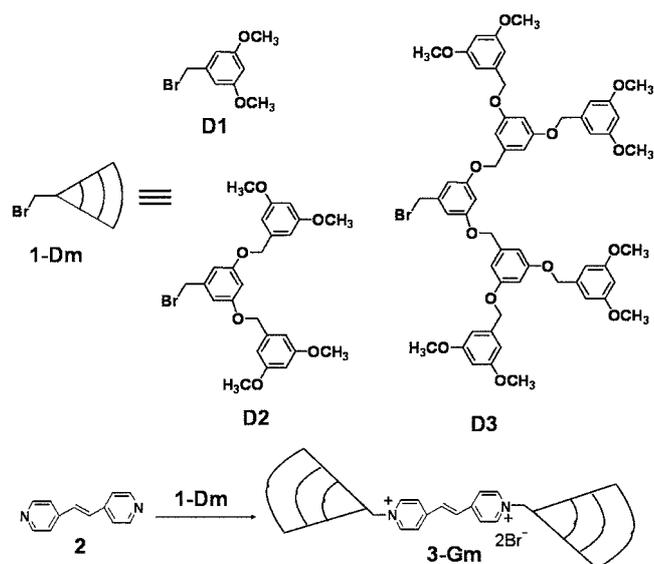


Figure 1. Structures of benzyl bromide dendrons **1-Dm** ($m = 1, 2,$ and 3 : generation of dendron) and schematic representation of dendrimers **3-Gm**.

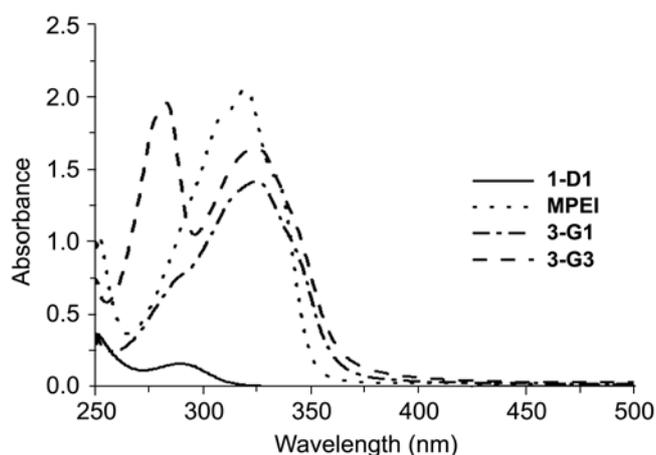


Figure 2. Absorption spectra of **3-G1**, **3-G3**, **MPEI**, and **1-D1** in DMSO-acetonitrile (4 : 1) solution at 298 K.

dimethylsulfoxide (3 : 1) solution at 298 K is shown in Figure 2, where the spectra of its component units (*N,N'*-dimethyldipyridyliumylethylene diiodide (**MPEI**) and dendron **1-D1**) are also displayed for comparison. The spectrum in **3-G1** is dominated by the strong absorption of dipyridyliumylethylene ($\lambda_{\max} = 324$ nm), with some contribution from the 1,3-dialkoxybenzene units around 283 nm. The spectrum in **3-G3** is characterized by the strong absorption of dipyridyliumylethylene ($\lambda_{\max} = 324$ nm) with the strong absorption of the 1,3-dialkoxybenzene units around 283 nm. These result is well-matched with the increasing number of 1,3-dialkoxybenzene units goes to higher generations. Therefore, as the dendrimer generation increases, the intensity of the absorption spectrum around 283 nm is raised because of the increasing number of 1,3-dialkoxybenzene units. But it is observed that a linear correlation of the molar absorption coefficient at 283 nm with the number of the 1,3-dialkoxybenzene units is not fully satisfied. This result suggests that there are interactions between the 1,3-dialkoxybenzene units and dipyridyliumylethylene unit which may be assigned to charge-transfer (CT) transitions from the 1,3-dialkoxybenzene electron-donor units to dipyridyliumylethylene electron-acceptor core in dendrimers.⁴⁻⁶ This interaction could be confirmed by the fact that the dendrimers exhibit a broad and weak absorption tail at around 376 nm (Figure 2).

In summary, we have demonstrated the high yielding and first synthesis of dendrimers *via* the convergent method which contain the dipyridyliumylethylene unit as photoresponsible and redox-active unit at core. Further studies on

the photochemical and electrochemical behaviors of core group in dendrimer are currently in progress.

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- 3-G1**: 98% yield; ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.86 (s, 12 H), 5.84 (s, 4 H), 6.66 (s, 2 H), 6.87 (s, 4 H), 8.27 (s, 2 H), 8.48 (d, *J* = 10.3 Hz, 4 H), 9.36 (d, *J* = 10.2 Hz, 4H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 161.9, 151.7, 145.9, 136.8, 135.0, 126.7, 107.9, 101.5, 63.8, 56.3; MS (FAB): *m/z*: 484.243 [M - 2Br⁻].
- 3-G2**: 95% yield; ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.82 (s, 32 H), 5.13 (s, 8 H), 5.82 (s, 4 H), 6.53 (m, 4 H), 6.65 (m, 8 H), 6.81 (m, 2 H), 6.91 (m, 4 H), 8.22 (s, 2 H), 8.44 (d, *J* = 11.3 Hz, 4 H), 9.28 (d, *J* = 11.1 Hz, 4H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 161.4, 160.7, 151.6, 145.9, 139.8, 136.9, 135.0, 126.6, 108.9, 106.4, 103.3, 100.2, 70.2, 63.8, 56.1; MS (FAB): *m/z*: 1028.014 [M - 2Br⁻].
- 3-G3**: 86% yield; ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.81 (s, 48 H), 5.11 (s, 24 H), 5.83 (s, 4 H), 6.52 (m, 8 H), 6.66 (m, 16 H), 6.74 (br, 4 H), 6.76 (br, 8 H), 6.83 (br, 2H), 6.95 (m, 4 H), 8.16 (s, 2 H), 8.40 (d, *J* = 9.9 Hz, 4 H), 9.31 (d, *J* = 9.9 Hz, 4H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 161.4, 160.8, 160.3, 151.6, 145.9, 140.1, 139.8, 136.9, 134.9, 126.6, 108.9, 107.5, 106.2, 103.2, 102.0, 100.2, 70.2, 70.0, 63.8, 56.0; MS (MALDI-TOF): *m/z*: 2117.381 [M - 2Br⁻].