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Nanomaterials of Triazine-Based Dendrons: Convergent Synthesis and Their Physical Studies

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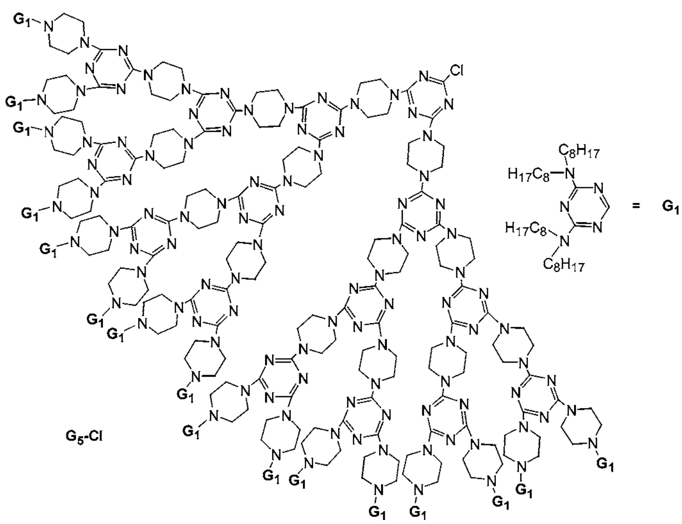
ABSTRACT



Without employing protection and deprotection processes, two series of triazine-based dendrons were efficiently prepared by a convergent method and fully characterized; their physical properties, including acidic, thermal, electrical, and optical stabilities were also studied.

Dendrimers, generally containing central cores, bridging units, and terminal functionalities, are branchlike molecules and therefore possess three-dimensional or branched structures. They have unusual properties such as multiple functionality and monomolecular weight and have been extensively investigated in recent years.[1] Particularly, the multiple functionality allows dendrimers to be involved in many applications such as catalytic materials,[2] molecular micelles,[3] light-harvesting molecules,[4] transportation of drugs,[5] liquid crystals,[6] initiators of macromolecules,[7] sensors,[8] porous and interfacial materials,[9,10] and conjugated and self-assembled molecules.[11,12] However, the preparation of functional dendrimers is generally difficult and tedious, as

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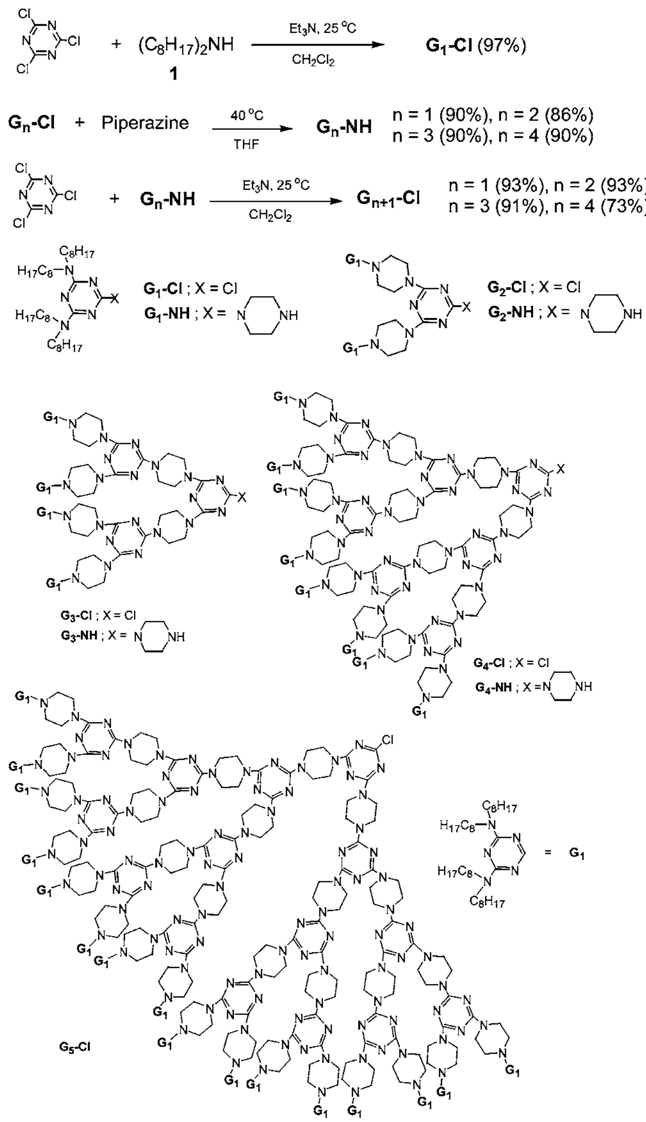
protecting and deprotecting processes are always needed during the synthesis and extremely low solubility of the dendrimers may be encountered for rigid or conjugated systems.[1,11] However, dendrimers are still interesting and challenging because of their versatile and potential applications. We thus rationally designed a new type of dendron (dendrimer-like molecules) with good thermo- and electrostabilities as these two properties are first considered on designing materials in application of optical and electrical areas.[12] Particularly, our new dendrons can be efficiently prepared in good yields and no protecting and deprotecting steps are needed during the convergent processes. Now we wish to report our primary results.

It has been well-known that the overall effect from the electrodonating and electrowithdrawing substituents on the aromatics significantly influences their relative reactivity. Therefore, we may selectively allow two or three equivalents of amines to react with cyanuric chloride at different temperatures and consequently isolate the corresponding adducts as reported by Simanek and Takagi.[13] A portion of 2.2 equiv of dioctylamine **1** was thus treated with cyanuric chloride in CH_2Cl_2 containing an excess of the triethylamine at 25 °C to give compound **G$_1$-Cl** in 97% yield after chromatography, which was further allowed to react with 3 equiv of piperazine in THF at 40 °C to give compound **G$_1$-NH** in 90% yield after chromatography (Scheme 1). Surprisingly, no disubstituted product (**G$_1$-N-G$_1$**) was observed, which may result from the transannular effect as indicated in the literature together with the steric effect from the dialkyl moieties.[14] Compound **G$_2$-Cl** was also obtained from reaction of compound **G$_1$-NH** with cyanuric chloride in a similar manner. Analogously, compounds **G$_2$-NH**, **G$_3$-Cl**, **G$_3$-NH**, **G$_4$-Cl**, **G$_4$-NH**, and **G$_5$-Cl** were prepared in excellent yields by alternatively incorporating triazine and piperazine functionalities on repeating the previous procedures. It is worthwhile to point out that there are no protecting and deprotecting processes involved during the preparation of the dendrons **G$_n$-Cl** (n = 1, 2, 3, 4, 5) and **G$_n$-NH** (n = 1, 2, 3, 4). Also, the reaction was carried out under mild conditions and no specially dried solvents were needed, as the reactivity of the amine is much higher than water and a small amount of moisture in the solvent did not obviously affect the reaction results. Compounds **G$_1$-Cl** and **G$_1$-NH** are liquids and are therefore characterized only by ^{1}H NMR and high-resolution mass spectroscopy. Compounds **G$_n$-Cl**, **G$_n$-NH** (n = 2, 3, 4), and **G$_5$-Cl** are characterized by ^{1}H NMR, elemental analysis, and mass spectroscopy. The mass spectrum of **G$_5$-Cl**, obtained by MALDI-TOF, is demonstrated in Figure 1. Clearly, the peaks at 12 694.8 and 12 739.7 arising from the $(M + Na)^+$ and $(M + 3Na)^+$ ions, respectively, were observed. Generally, a Na^+ ion from the sample holder was present during the characterization process of the mass spectroscopy.[8] **G$_5$-Cl** was further characterized by microanalysis, and the errors for calculated and experimental percentages for C, H, and N were within 0.08%.

Dendrons **G$_n$-Cl** and **G$_n$-NH** (n = 1, 2, 3, 4) are reasonably soluble in organic solvents such as CH_2Cl_2 and THF, and the solubility decreases gradually when n increases. This may

Scheme 1. Preparation of Compounds **G$_n$-Cl**, **G$_n$-NH**, and **G$_5$-Cl**[a]



[a] n = 1, 2, 3, 4.

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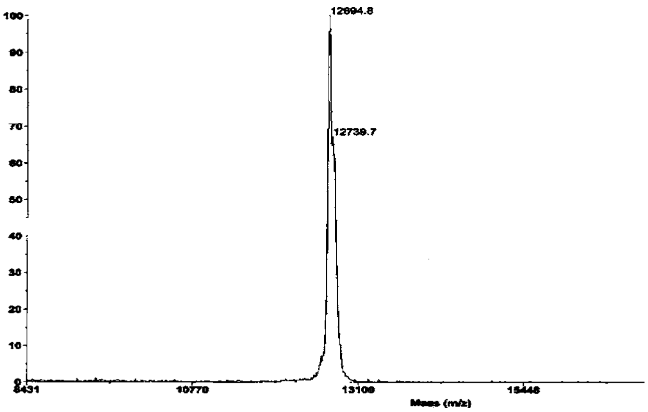


Figure 1. Mass spectrum of **G_5-Cl (**obtained by MALDI-TOF).

result from the increasing of the rigid−flexible ratio in the dendrons. However, the solubility of **G_5-Cl** is better than that of **G_4-Cl** and is comparable with that of **G_3-Cl**. To understand this behavior, the conformations of **G_5-Cl** and **G_4-Cl** were simulated by the CAChe program using the MM2 model in the gas phase. The starting conformation of **G_1-Cl** was first established by combination of one planar triazine with two dioctylamine moieties and then optimized. The conformation of **G_1-NH** was then obtained by combination of the optimized **G_1-Cl** with piperazine in chair form. Similarly, the conformation of **G_2-Cl** was obtained by combination of the planar triazine with two optimized **G_1-NH** units. In a similar manner, the optimized conformations of **G_4-Cl** and **G_5-Cl** were thus obtained and are demonstrated in Figure 2a and 2b, respectively. The conformation of **G_4-Cl** is rather coplanar. However, the **G_5-Cl** molecule is congested by two **G_4-N** moieties and thus possesses a staggered conformation. This should clearly explain the different solubilities of the **G_4-Cl** and **G_5-Cl** molecules in organic solvents. Generally, the introduction of the long alkyl chain solves the problem of low solubility, which may be encountered in rigid dendritic systems.

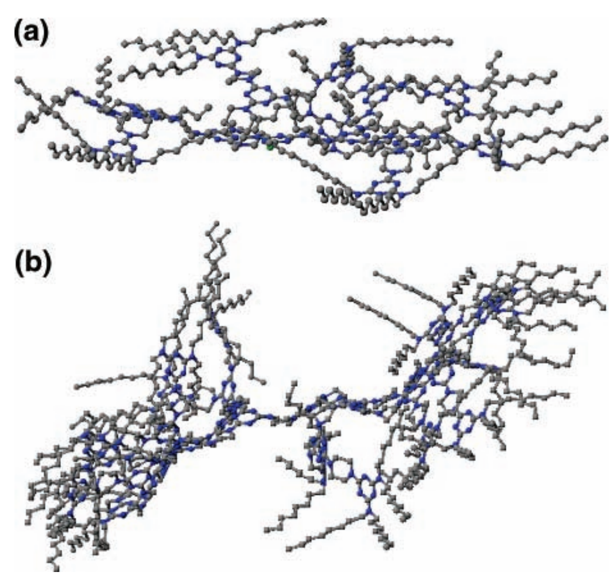
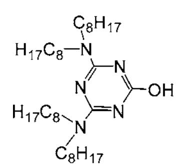


Figure 2. (a) Molecular conformation of dendron **G_4-Cl** (N, blue; C, gray; hydrogens are omitted for clarity). (b) Molecular conformation of dendron **G_5-Cl** (N, blue; C, gray; hydrogens are omitted for clarity).

Compound **G_5-Cl**, representing this series of molecules, was also investigated by TGA, and surprisingly, this compound is stable and only starts to decompose at ∼300 °C. To understand the optical and electrical properties of the dendrons, **G_3-Cl** in CH_2Cl_2 representing this series of molecules was also investigated by UV spectroscopy and electrovoltammetry. Interestingly, no significant absorbance beyond 280 nm was observed in the UV spectrum, which is important in the application of optical areas. Also, no significant decomposition was observed between 1.3 and −2.0 V in the electrochemical study. In the reductive cycle, the cyclic voltammograms of **G_3-Cl** in CH_2Cl_2 are very similar to that of the blank experiment. It is thus regarded that the triaminotriazine unit is an electron-rich moiety, and thus, no further reduction takes place at −2.0 V. However, the triaminotriazine unit is oxidized at ∼1.3 V and subsequently decomposes. Moreover, compound **G_4-NH** was found to be unstable in acidic media; after this compound was stirred in THF at pH = 2 for 2 h, the decomposing residues were extracted with CH_2Cl_2 and then characterized by GC-mass spectroscopy. The resulting spectrum is complicated, but two peaks at 577 and 355 are clearly observed, which should result from the decomposed moieties **2** and **3**. Clearly, in acidic solution, the lone pair of the nitrogen is protonated and increases the reactivity of the triazine ring. Subsequently, the water molecule in the solution reacts with the dendron, leading to components **2** and **3**. Interestingly, **G_4-NH** was not observed to decompose even at pH = 1 or 2 in 70 min. However, once it decomposes, the decomposing rate increases dramatically, and this may result from the further production of acid molecules during the decomposing process. Also, the decomposing rate was quite slow when the solution was maintained at pH = 3−7.



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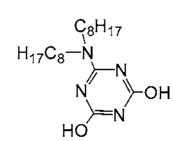

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In summary, we efficiently prepared two series of new dendrons, **G_n-Cl** (n = 1−5) and **G_n-NH** (n = 1−4). Noteworthy is that the protecting and deprotecting processes are not needed during this convergent process. These compounds also contain functionalities, NH and Cl, for further reaction. By investigating a representative sample, they appear to possess stable thermo- and electroproperties together with low absorbance beyond 280 nm in the UV spectrum. Therefore, the new dendrons can be useful architectures for connecting functional groups with special properties in the area of modern electro- and optomaterials, such as OLED and LCD.

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Supporting Information Available: Description of synthetic procedures, the computational and decomposing processes, compound spectra, and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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