# Turbine Shape Organotin Dendrimers: Photophysical Properties and Direct Replacement of Sn with Pt

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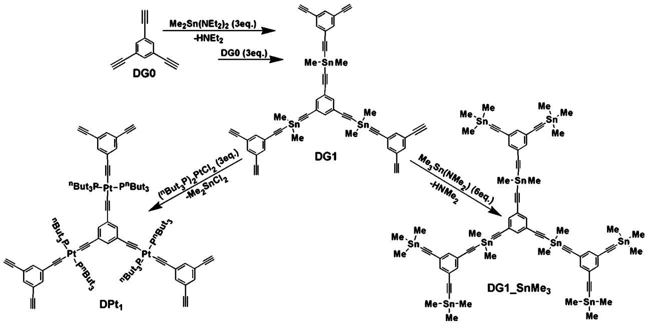
Designing new dendritic macromolecules continues to be a topical area of research due to their unique properties and the possibility to tailor and control their overall structure using a variety of molecules that constitute their template core and backbone.[1] Hyperbranched architectures containing rigid conjugated organic backbones are of considerable interest due to their potential in designing novel materials by exploiting their photophysical, electronic, and optical properties.[2,3] We were interested in exploring the structure of dendrimers that will evolve from 1,3,5-triethynylbenzene (TEB) at the template core as well as in the backbone, linked by dimethyltin moieties, and the role of rigid molecular structure and geometrical requirements of the linking unit, in shaping the overall structure of these dendrimers. In this manuscript, we report a simple methodology to synthesize TEB-based dendrimers and an evaluation of their structure that develops into a turbine shape, with benzene rings arranged in a fashion to create sandwich type cavities. Organic donors placed at the periphery of conjugated backbones are known to enhance $\pi$-conjugation in their backbone.[3] We demonstrate here that inorganic groups such as $Me_3Sn$ provide a similar electronic donating effect and can significantly influence the photophysical properties of these hyperbranched macromolecules. The versatility of these macromolecules in synthesizing dendrimers containing transition metal moieties in the backbone is demonstrated by a direct substitution of dimethyltin links with square planar platinum centers, upon reaction with $(^nBu_3P)_2PtCl_2$. This eliminates the need of a catalyst in the synthesis of such organometallic dendrimers.

The divergent synthetic methodology used to construct TEB based dendrimers is based on acid−base hydrolytic chemistry[4] of aminostannanes with molecules containing terminal acetylenes. It involved controlled reiterative reaction of molar equivalents of TEB and bis(diethylamino)dimethyltin [$Me_2Sn(NEt_2)_2$] (Scheme 1).

The only byproduct in the reaction is a low boiling amine that is removed under vacuum, and the resulting dendrimers are purified by extraction into benzene. The capping of each dendrimer generation with $Me_3Sn$ can be achieved by reacting with an appropriate amount of $Me_3Sn(NMe_2)$ (Scheme 1).

A detailed investigation of the structure of these dendrimers, using the molecular mechanics MM$^+$ method and the PM3 semiempirical molecular orbital theory,[5] shows that the TEB units adopt a completely rigid flat structure and the tin centers are most stable when a tetrahedral structure around them is retained. For the latter arrangement, and to reduce steric hindrance, the TEB units in the upper layers do not stay in the same plane as the TEB unit at the template core. For example, the first generation dendrimer adopts a turbine shape in which the three peripheral TEB arms tilt away from the plane in the same direction, at identical dihedral angles (∼45°) around the core arms (Figure 1). In the second generation, the next layer of TEB and Sn centers orient in the same fashion with similar dihedral angles. This leads to an outward growth of each arm away from the center, without back folding in the space between the arms. The additional layer in the third generation dendrimer grows in a similar relationship to **DG2**. The sustained dihedral angles allow the arms to grow without any crowding that would prevent growth. Because of the larger size of the arms in **DG3**, a more defined three-dimensional structure develops that resembles a turbine, with the outer benzene ring of an arm coming on top of the arm next to it, at a distance of approximately 20 Å (Figure 1). This creates sandwich type cavities in between the turbine arms that could act as potential host sites for molecular encapsulation of small guest molecules, through $\pi-\pi$ interactions.

**Scheme 1. Synthesis of the First Generation Dendrimer (DG1), Capping with $Me_3Sn$ and Replacement of Sn with Pt**



The average diameters of these dendrimers were found to be 22, 40, and 52 Å for generations 1−3, respectively. Interestingly, these sizes are larger, by an average of 7 Å, than corresponding dendrimers with more flexible backbones, such as 3,5-dihydroxybenzyl alcohol (DHBA).[6a] This demonstrates that the rigidity of TEB and the reinforced tetrahedral geometry around tin do not permit many options for the TEB arms to move or rotate. In fact, a slight rotation around the tin linkages causes a dramatic increase in the energy of the most stable dendrimer structure. On the other hand, in more flexible dendrimer back bones, the arms can be rotated around the linking unit with only a slight increase in energy.[6]

The photophysical properties of the TEB-based dendrimers were studied using UV−vis absorption and fluorescence spectroscopies (Table 1). The absorption spectrum of TEB (**DG0**) shows $\lambda_{max}$ at 305 nm, and a fluorescence emission band ($\lambda_{max}$) at 336 nm with a quantum yield of 6%. The emission spectrum of the first generation dendrimer (**DG1**) showed only a small red shift; however, its quantum yield almost doubled (11%). The emission spectrum of the second generation dendrimer (**DG2**) showed similar emission $\lambda_{max}$ and a slightly better quantum yield (13%) than the first generation. The same trend was observed for the third generation dendrimer (**DG3**).

Recent studies have shown that the presence of dipolar units consisting of donor (OMe) and acceptor (C≡C) groups enhances photophysical properties and fluorescence quantum yields of star-shaped oligomers that originate from the TEB core.[3] Interestingly, the presence of $Me_3Sn$ groups at the periphery,

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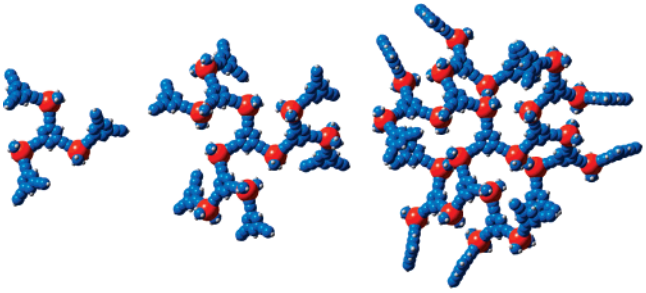

**Figure 1.** PM3-optimized structures of TEB dendrimer generations 1−3.

**Table 1. Photophysical Data of DG0 to DG3 and Their Capped Forms (DG0−SnMe$_3$ to DG3−SnMe$_3$) in Benzene at Room Temperature**

| dendrimer | $\phi_f$[a] | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm) |
|---|---|---|---|
| **DG0** | 0.06 | 305 | 336 |
| **DG1** | 0.11 | 308 | 345 |
| **DG2** | 0.13 | 308 | 346 |
| **DG3** | 0.17 | 308 | 346 |
| **DG0−SnMe$_3$** | 0.22 | 311 | 346 |
| **DG1−SnMe$_3$** | 0.30 | 314 | 348 |
| **DG2−SnMe$_3$** | 0.32 | 314 | 349 |
| **DG3−SnMe$_3$** | 0.35 | 314 | 349 |

[a] Quantum yield is calculated relative to quinine sulfate ($\phi_f = 0.55$ in 0.1 M $H_2SO_4$).

and symmetrically placed $Me_2Sn$ links in the backbone of the dendrimers reported here, shows a similar effect to that of organic donors. This is demonstrated by the red shift in the absorption/emission spectra and the increase in quantum yields of TEB dendrimers, compared to the TEB molecule. For example, capping of TEB (**DG0**) with trimethytin at its periphery (**DG0−SnMe$_3$**) led to a red shift in its absorption and emission spectra, and its quantum yield was found to be almost 4 times higher (22%) than that of **DG0** (Table 1). It clearly suggests that the trimethytin moiety is acting as a donor and enhances $\pi$-conjugation in the molecule. These results were further supported by Mulliken charge[7] calculations on the atoms of the core molecule (**DG0**) and its trimethyltin capped analogue (**DG0−SnMe$_3$**). Mulliken charges provide an estimation of partial atomic charges. For example, in **DG0**, the terminal carbon in acetylene has a Mulliken charge of −0.158 e, which increases to −0.457 e upon capping with $SnMe_3$ (**DG0−SnMe$_3$**). This indicates that the acetylenic carbon becomes more electron rich upon binding to Sn. Similarly, upon capping the first generation dendrimer with trimethyltin (**DG1−SnMe$_3$**), a larger red shift in the absorption maxima and an increase in the quantum yield to about 30% were observed (Table 1). Capping of dendrimers of generations 2 and 3 with trimethyltin (**DG2−SnMe$_3$** and **DG3−SnMe$_3$**) led to a similar increase in their quantum efficiencies.

The presence of dimethyltin moieties in the backbone of the dendrimers enhances their quantum efficiencies to some extent and causes a red shift in the absorption spectra by about 5 nm. Since a dimethyltin group in the backbone of the dendrimer is placed between two acceptor (C≡C) moieties, its donating effect is shared equally in both directions. On the other hand, when trimethyltin groups are added to the peripheries of the dendrimers, a larger red shift in the absorption spectrum is observed and the quantum yields are enhanced to almost 6-fold, suggesting that terminally substituted $Me_3Sn$ groups have a stronger unidirectional donor effect.

Dendrimers containing transition metal centers in the backbone continue to attract great interest due to their applications in catalysis, photonics, etc.[8] Acetylenic molecules ligated to Sn are known to undergo a metathesis reaction with transition metal halides, and the latter reaction has been demonstrated to be a useful methodology to synthesize linear organometallic polymers.[9] We were intrigued by the possibility of replacing Sn moieties directly in the backbone with transition metal centers, yielding an attractive route to organometallic dendrimers. In a preliminary investigation, we attempted the reaction of the first generation dendrimer (**DG1**) with 3 equiv of $Cl_2Pt(P^nBu_3)_2$ at room temperature. It led to the replacement of $Me_2Sn$ moieties in the dendrimer with $Pt(P^nBu_3)_2$. Such platinum−acetylide dendrimers have been prepared earlier using CuI and $NEt_2H$ base-catalyzed condensation reactions of metal halides with acetylenic compounds.[10] The direct substitution of the Sn moiety in the dendrimers with platinum centers without the need of a catalyst offers potential in tailoring the backbone structure and the resulting properties of the dendrimers described here. We are currently studying the details of this substitution reaction and will subsequently expand the scope of this methodology.

We have demonstrated that a rigid molecular structure of the repeat unit and the geometric constraints of the linker can significantly influence the evolving hyperbranched structure of the dendrimers. The 1,3,5-triethynylbenzene unit at the template core assumes a flat morphology with the subsequent TEB molecules in the higher generations bending away from each other. It leads to a turbine shape with the benzene rings in a sandwich type structure. The inorganic entities ($SnMe_3$) present at the periphery of these dendrimers act as donors, which enhances $\pi$-conjugation leading to improved quantum yields. The direct metathesis of the $Me_2Sn$ links with $Pt(P^nBu_3)_2$ can be carried out upon reaction with $Cl_2Pt(P^nBu_3)_2$, and it offers a useful synthetic methodology to construct organometallic dendrimers without the need for a catalyst.

**General Procedure for the Dendrimers Synthesis.** In a typical iterative reaction sequence, a solution of 1 equiv of **DG0** in dry THF was added dropwise over a period of almost 3 h to an ice-bath cooled solution of 3 equiv of $Me_2Sn(NEt_2)_2$ in THF. The mixture was left to stir for 1 h, warmed to room temperature, and then added to a solution of 3 equiv of **DG0** in THF, in a dropwise fashion over a period of 6 h, and left to stir overnight. After removal of the solvent under vacuum, the first generation dendrimer was extracted into benzene and the removal of solvent yielded a yellowish white solid. The synthesis of the second and third generation dendrimers was done in a similar fashion, by continuing the building over generation 1 and 2, respectively. For capping with $SnMe_3$, to a solution of **DG0** in THF, 3 molar equiv of $Me_3Sn(NMe_2)$ were added. The solution was left to stir at room temperature overnight. The solvent was subsequently evaporated, and the resulting product was extracted into benzene to yield the desired product in quantitative yields. A similar method was adopted for generations 1, 2, and 3 using 6, 12, and 24 molar equiv of $Me_3Sn(NMe_2)$, respectively. The replacement of Sn by Pt in **DG1** was done by mixing 1 equiv of the dendrimer with 3 equiv of $(^nBu_3P)_2PtCl_2$ in THF. The mixture was left to stir at room temperature for 48 h. The solvent was evaporated, and the resulting solid was washed several times with hexanes to yield the desired product (**DPt1**). For details of all experimental procedures and characterization data of all the products, see the Supporting Information.

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**Supporting Information Available:** Synthetic details and characterization data of dendrimers, their $SnMe_3$ terminated analogs, and dendrimer in which tin is replaced with platinum in the backbone; scheme showing structures of dendrimers; MALDI-TOF mass spectra of generation 1−3 dendrimers and mass spectrum of dendrimer terminated with $SnMe_3$; $^{31}P\{^1H\}$ NMR spectrum of platinum dendrimer; and fluorescence spectra of dendrimer generation 0 and its capped form. This material is available free of charge via the Internet at http://pubs.acs.org.

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