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# Design and Synthesis of Nonconjugated Monodendrons with Triarylamine Repeating Units

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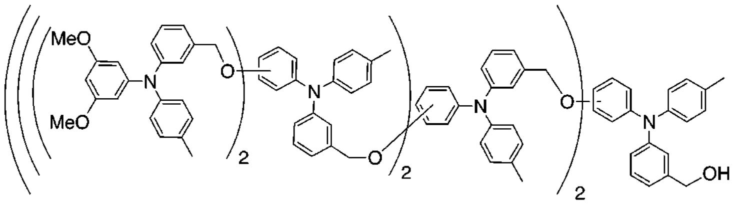
## ABSTRACT



**Design and synthesis of new monodendrons with triarylamine repeating units, which are potentially useful in charge transport applications, are described. The triarylamines are connected through a nonconjugated linkage to facilitate independent electronic tuning of the monomer units.**

Controlling the vectorial transport of energy and electrons in organized molecular assemblies has been of current interest due to the potential applications of these architectures in artificial photosynthesis,[1] photovoltaic cells,[2] materials for optical data storage,[3] thin-film transistors,[4] and electroluminescent materials.[5] The required functional group organizations have been approached using linear arrays of porphyrins[6] and diimides[7] or other molecular assemblies such as liquid crystals,[8] zeolites,[9] polymers,[10] peptides,[11] and amphiphiles.[12]

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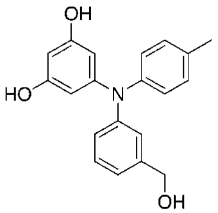
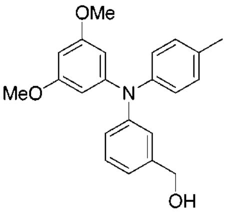
The unique architecture of dendrimers provides a new dimension for the precise placement of charge-transport units in a single molecule. Since dendrimers are highly branched macromolecules,[13] they offer control over the placement of functional groups in higher dimensions than that offered by linear arrays. Dendrimers should also be advantageous for the funneling of charges from the core to the periphery, because the number of functional units doubles with each layer. Several photophysical studies based on dendritic architectures have been reported over the past few years.[14] However, in most of these cases, the light harvesting functional groups are incorporated as the core unit or as the peripheral units, perhaps largely due to the high synthetic facility with which these arrays can be obtained. To exploit all the architectural features offered by dendrimers, it is advantageous to build them where these functional groups are incorporated as the repeating units.[15] There have been a few recent reports where triarylamine units were incorporated as the repeating units of dendrimers.[16] In all these cases, the backbone of the dendrimer was chosen in such a way that the triarylamines are conjugated with each other. The presence of a conjugated backbone has its obvious merits for charge-transport studies. However, it is interesting to design dendrimers with nonconjugated triarylamine units, in which facile charge transport among the repeating units is maintained through the dendrimer's backbone. The advantage of such a molecular scaffold is that the frontier orbital energies of the individual monomer units can be independently tuned. This provides the pathway for the design of dendrimers with energy level gradients that can direct the vectorial transport of charges. Since the charge transporting ability of Fréchet-type benzyl ether backbones has been demonstrated[14d,k] and since these dendrimers can be synthesized with high facility using a convergent approach,[17] we targeted benzyl ether based dendrons with triarylamine repeating units.

For the synthesis of benzyl ether based monodendrons, the building blocks require two phenolic moieties and one benzyl alcohol moiety. Thus, the targeted repeating monomer is represented by structure **1** in Figure 1. The synthetic requirements could have been fulfilled with a much more symmetrical structure in which the three functional groups are at the *para*-positions. However, we envisioned that it would be advantageous to have the current design for two practical reasons: (i) It is desirable to leave one of the aryl rings free from the dendrimerizable functional groups in order to gain the ability to tune the frontier orbital energies of the building-block units. In the present case, that ring is substituted with a methyl group. (ii) The presence of a strong electron-donating group *para* to a benzyl bromide moiety could render the molecule highly reactive and therefore possibly unstable.[18] Therefore, the hydroxymethyl group is placed *meta* to the amino moiety. Also note that in the convergent synthesis the peripheral monomer unit should have the two phenolic moieties in its protected form. Therefore, structure **2** was targeted as the peripheral unit (Figure 1).



**1**



**2**

**Figure 1.** Structures of the triarylamine monomer units.

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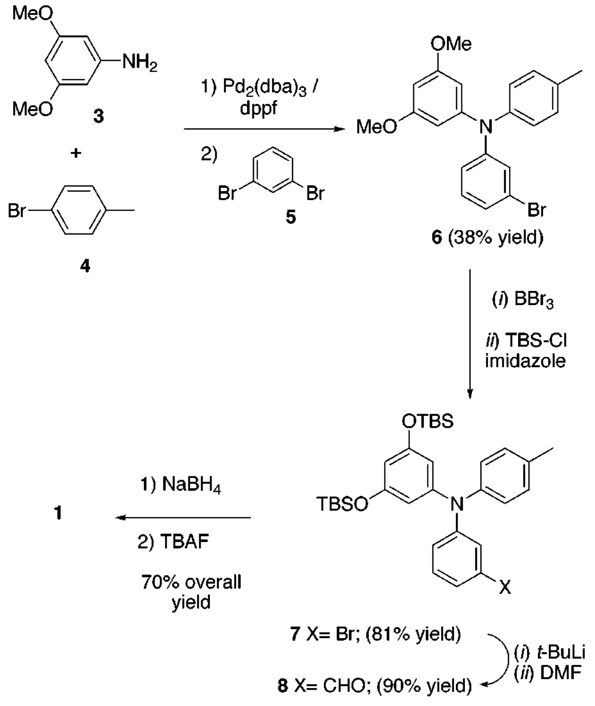
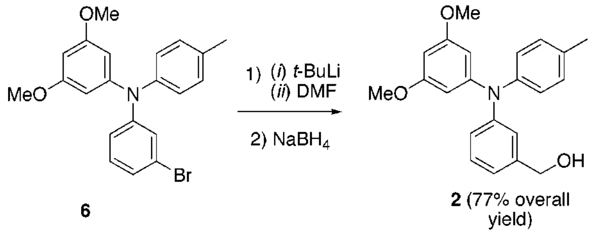
(18) Note that the benzyl alcohol moiety will be converted to a benzyl bromide during the dendrimer synthesis (vide infra).

The triarylamine units were assembled using the one-pot version[19] of the palladium-catalyzed C−N bond-forming methodology.[20] Accordingly, 3,5-dimethoxyaniline (**3**) was treated with *p*-bromotoluene (**4**) in the presence of tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$) and bis(diphenylphosphino)ferrocene (dppf) with sodium *tert*-butoxide as the base. The progress of the reaction was monitored by thin-layer chromatography, and upon completion of the reaction, excess 1,3-dibromobenzene (**5**) was added as the second aryl bromide to afford the triarylamine product **6** in 38% overall yield. Compound **6** was treated with boron tribromide to deprotect the methoxy groups and afford the corresponding diphenolic product in 91% yield. These phenolic moieties were then reprotected with *tert*-butyldimethylsilyl (TBS) groups to afford the corresponding disilyl ether **7** in 90% yield. At this juncture, the bromoarene was converted in 90% yield to the corresponding aryl carboxaldehyde **8** by treatment with *tert*-butyllithium followed by DMF. The aldehyde was reduced using sodium borohydride to afford the corresponding hydroxymethyl compound, followed by desilyation with TBAF to obtain the targeted building block unit **1**. The synthetic steps are outlined in Scheme 1. The peripheral monomer **2** was synthesized from **6** in 77% overall yield, by converting the bromo functionality to a hydroxymethyl group using the methodologies described above (Scheme 2).

**Scheme 1.** Synthesis of **1**



**Scheme 2.** Synthesis of **2**



The syntheses of the monodendrons from compounds **1** and **2** were carried out following the convergent synthetic approach introduced by Fréchet.[17] Accordingly, the hydroxymethyl group of **2** was treated with triphenylphosphine and carbon tetrabromide to afford compound **9** in 69% yield. Two equivalents of the bromomethyl compound **9** were treated with the diphenolic compound **1** in the presence of potassium carbonate and 18-crown-6 to afford the 3-mer-OH **10** in 63% yield. The hydroxymethyl substituent at the core of **10** was converted to the bromomethyl moiety followed by reaction with 0.5 equiv of the repeating unit **1** to afford the 7-mer-OH **11** in 58% overall yield. These two steps were repeated to convert the 7-mer-OH **11** to the 15-mer-OH **12** in 18% overall yield, as shown in Scheme 3.

The triarylamine monodendrons were characterized by NMR and matrix-assisted laser-desorption time-of-flight (MALDI-ToF) mass spectrometry. The $^1$H NMR shift of the methoxy groups of the peripheral monomer and the benzyl methyl groups were useful in the characterizations of the monodendrons. The chemical shift of the benzyl methyl groups were consistently around 2.2−2.3 ppm, whereas that of the methoxy groups was 3.5 ppm. The relative integration between these two areas was a useful diagnostic tool for characterizing the generation of the dendrons. The conversion of the hydroxymethyl group to the bromomethyl moiety was not clearly identifiable with $^1$H NMR, since the chemical shifts of all the protons were similar, including that of the methylene group at the core. However, this conversion was monitored by thin-layer chromatography and further confirmed by MALDI-ToF mass spectrometry. Also, the possibility of alkylating just one of the two phenolic groups in **1** posed difficulties in unambiguously assigning the structures of these dendrons by NMR, because the differences in relative integration of the $^1$H NMR peaks between this possibility and the expected monodendrons were small. However, MALDI-ToF mass spectra confirmed the structures of **10**−**12**, with no peaks for the corresponding monosubstituted dendrons.

In summary, syntheses of monodendrons with triarylamine repeating units and nonconjugated benzyl ether connectivities were realized. It is noteworthy that the resultant monoden-

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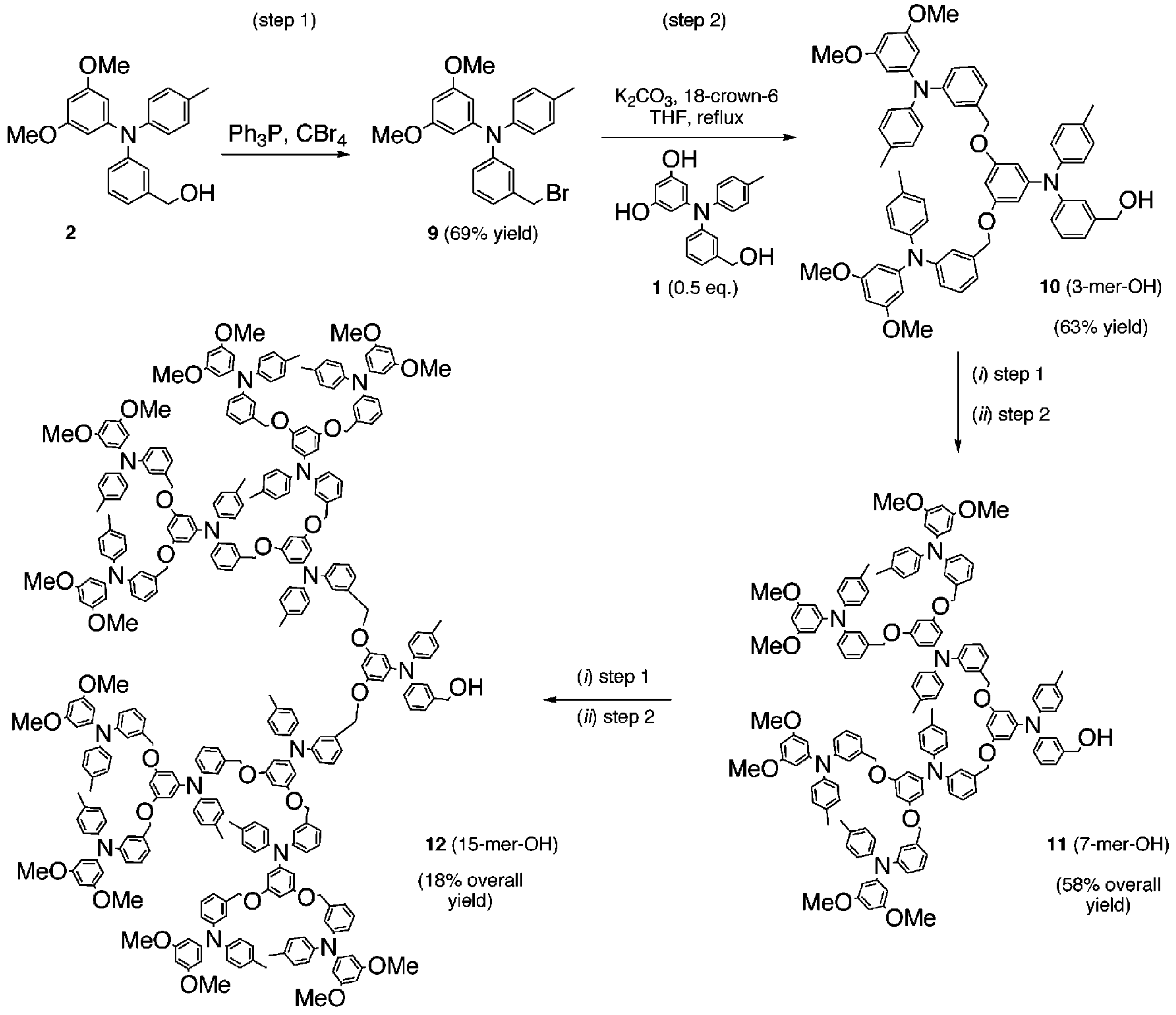
**Scheme 3.** Synthesis of Triarylamine Monodendrons



drons are soluble in a variety of organic solvents in contrast to the analogous conjugated monodendrons.[16a,b] This facilitates solution photophysical studies, which will be reported in the near future.

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**Supporting Information Available:** Experimental details and characterization data for all the compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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