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Facile Iterative Synthesis of Biphenyl Dendrons with a Functionalized Focus

Ellen J. Wren, Xin Wang, Anthony Farlow, Shih-Chun Lo, Paul L. Burn,* and Paul Meredith

Centre for Organic Photonics & Electronics, The University of Queensland, School of Chemistry & Molecular Biosciences, Chemistry Building, Queensland, Australia, 4072

p.burn2@uq.edu.au

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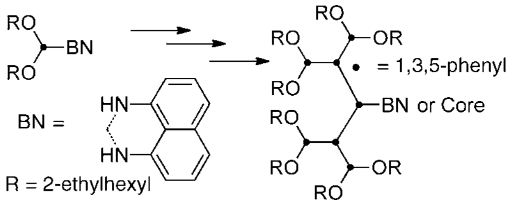
ABSTRACT



An iterative procedure gives 1,3,5-phenyl-linked dendrons of up to the fourth generation and enables the formation of different generations of iridium(III) complex-cored dendrimers. The convergent synthesis uses *N,N′*-1,8-napthyl-3,5-dibromophenylboronamide as the key building block. The iterative synthesis cycle involves deprotection of the boronamide-focused dendron to form a boronic acid and subsequent Suzuki coupling either with the *N,N′*-1,8-napthyl-3,5-dibromophenylboronamide to give the next dendron generation or with an activated core to form a dendrimer.

Optoelectronic materials fall into three main families, small molecules, conjugated polymers,[1] and dendrimers.[2] For dendrimer-based optoelectronic applications such as organic light-emitting diodes and solar cells, dendrimers with conjugated dendrons have proved to be the most successful.[2] Optoelectronic dendrimers are generally comprised of a core, dendrons, and surface groups. In the case of luminescent dendrimers that have been used in organic light-emitting diodes, the core is generally the emissive component with the dendrons acting as rigid spacers to control the intermolecular interactions that can lead to quenching of the luminescence.[3] The surface groups provide solubility and solution processability. A key feature of light-emitting dendrimers is that their properties are strongly dependent on dendrimer generation. Iterative procedures for the formation of higher-generation phenylacetylenyl,[4] stilbenyl,[5] polyphenyl,[6] and carbazolyl[7] dendrons are now well established, but the formation of different generations of simple 1,3,5-linked phenylene dendrons and their subsequent transformation to dendrimers has been less well studied.[8] Dendrimers with first- and second-generation 1,3,5-linked phenylene dendrons and iridium(III) complex cores have been used successfully to give OLEDs with external quantum efficiencies of up to 16% at a usable brightness.[9] The two generations of dendrimers were formed by complexation of dendronized ligands.[10] The synthesis of the second-generation dendrimer was hampered by the fact that the second-generation dendron could not be easily formed. Hence to achieve the synthesis of the second-generation dendrimer it was necessary to elaborate the ligand

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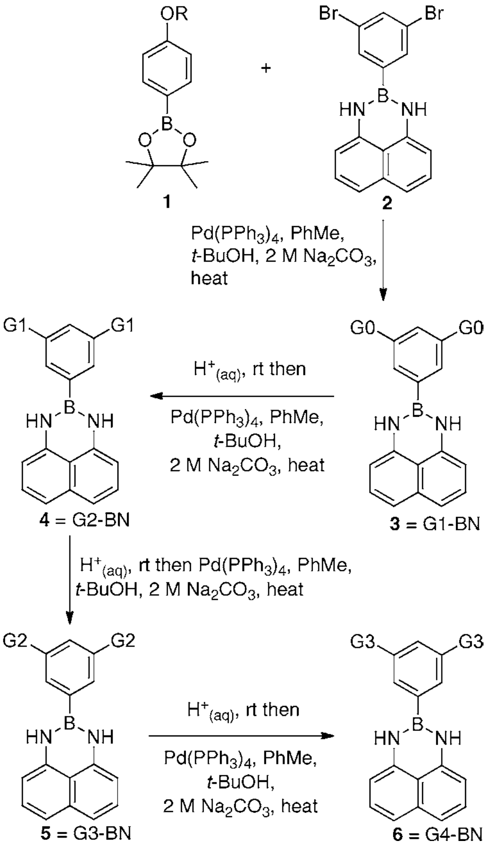
to enable the use of the first-generation dendron.[10] A simpler and more convergent method of preparing light-emitting dendrimers of higher generations is to have dendrons with reactive groups at their foci that can react with complementary functionality on the core. Herein we describe a two-step iterative method for the preparation of 1,3,5-linked phenylene dendrons up to the fourth generation with a protected boronic acid at their focus and their subsequent conversion to different dendrimer generations.

The basis of the strategy was the report that haloarylboronic acids protected with 1,8-diaminonapthalene, giving the corresponding boronic acid amides (boronamides), could undergo Suzuki cross-coupling reactions without polymerization. Deprotection of the boronamide then allowed further palladium-catalyzed cross couplings to build up more complex asymmetric aromatic oligomers.[11] Elaboration of this chemistry to form the 1,3,5-linked dendrons required the formation of *N*,*N′*-1,8-napthyl-3,5-dibromophenylboronamide **2**.

Boronamide **2** was formed in four consecutive steps. First, 1,3,5-tribromobenzene was metalated with *n*-butyllithium, and the carbanion was reacted with trimethylborate before subsequent hydrolysis with dilute hydrochloric acid to the corresponding boronic acid. Simple boronic acids are known to dimerize and trimerize, and hence in this work the corresponding acids were used immediately in the next step. The 3,5-dibromophenylboronic acid was reacted with 1,8-diaminonaphthalene in toluene heated at reflux for 5 h under Dean−Stark conditions to give **2** in a 59% overall yield for the four steps.

In previous work, it was found that 2-ethylhexyloxy surface groups gave the required solubility and processability for the 1,3,5-phenylene linked dendrons and dendrimers, and hence they were used in the current study.[10] The first step in the iterative procedure for forming the dendrons was the coupling of 2-[4-(2-ethylhexyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **1** with boronamide **2** to give the first-generation boronamide focused dendron **3**. This was achieved in a 79% yield using palladium(0) catalysis after 24 h. Each step of the iterative procedure then required the deprotection of the boronamide to the corresponding boronic acid and subsequent reaction with **2**. For example, the first-generation boronamide **3** was deprotected by reaction with aqueous acid to give the dendron with a boronic acid at its focus. The first-generation boronic acid was then coupled under palladium(0)-catalyzed conditions to give **4**, the second-generation dendron with a boronamide focus, in 65% yield. The cycle was repeated for the third-, **5**, and fourth-generation, **6**, dendrons to give yields of 77% and 36%, respectively (Scheme 1). It is important to note that increasing the reaction times caused a decrease in the yields.

Scheme 1. Iterative Cycle for Dendron Synthesis



The reported method for forming the iridium(III) complex-cored dendrimers with 1,3,5-linked phenylene dendrons involved the formation of the dendronized ligand and subsequent complexation to the metal cation.[10] The disadvantages of this route were that the method was only efficient if a first-generation dendron was used, and the yield of the complexation step was often low leading to waste of advanced intermediates. The alternative route is to couple the dendrons directly to the core complex, and we illustrate this process for green emissive phosphorescent iridium(III) complex cored dendrimers.

The synthesis of the first-generation *fac*-tris(2-phenylpyridyl)iridium(III) cored dendrimer is shown in Scheme 2, and the higher generations were formed in a similar manner. The boronamides were again deprotected to give the corresponding boronic acid, which was immediately used in the Suzuki coupling reaction with *fac*-tris[2-(5-bromophenyl)pyridyl]-iridium(III). For the first-generation dendrimer **7**, dendron **3** was deprotected with aqueous acid, and the boronic acid was then coupled using palladium(0) catalysis to the iridium(III) complex. The overall yield of **7** for the deprotection and three Suzuki couplings was 46%. This corresponds to an overall yield of 36% for the linear sequence from boronate ester **1**, which is higher than the 17% overall yield of **7** from **1** prepared via the shortest pathway using the dendronised ligand route.[10a] The second- and third-generation dendrons **4** and **5** were deprotected and reacted with the same core to

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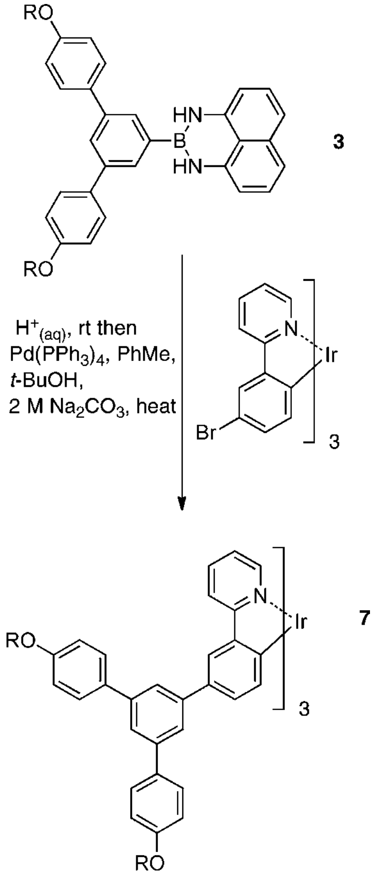
Scheme 2. First-Generation Iridium(III)-Cored Dendrimer Synthesis



give the equivalent second- and third-generation dendrimers (**8** and **9**) in 36% and 14% yield, respectively. The lower yield for the third-generation dendrimer, which is the highest generation of this type of dendrimer formed thus far, suggests that steric compression is becoming an important factor.

^{1}H NMR and thin-layer chromatography showed that dendrimers **7**, **8**, and **9** were pure, but careful analysis by gel permeation chromatography indicated that the first- and second-generation dendrimers contained small amounts (0.5−1.6%) of compounds that we believe are partially dendronized materials (dendrimers with one or two dendrons). In contrast, the third-generation dendrimer was pure by all criteria and had a polydispersity of 1.0. The first- and second-generation dendrimers have been previously reported to have photoluminescence quantum yields (PLQYs) in solution of 70% and 69%, respectively.[10a] In this work, the third-generation dendrimer **9** was found to have a PLQY of 89%. Interestingly, for **9** excitation in the dendron absorption region (310 nm) gave emission almost exclusively from the *fac*-tris(2-phenylpyridyl)iridium(III) core indicating that even for high generations intramolecular energy transfer can be efficient.

In conclusion, we have developed a simple iterative route to 1,3,5-linked phenylene dendrons that has been used to form up to the fourth generation. The strategy uses a masked boronic acid in the form of a boronamide. Successive Suzuki couplings and deprotections allow the dendrons to be formed in a convergent route, and the unmasked boronic acids can be used to couple to activated cores to give dendrimers of different generations.

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Supporting Information Available: Experimental procedures and characterization for compounds **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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