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Design and construction of supramolecular polysulfurated metallodendrimers with various shapes and sizes via coordination-driven self-assembly

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A B S T R A C T

A new family of 120° polysulfurated dipyridine donors have been successfully designed and synthesized, from which a series of novel rhomboidal and hexagonal supramolecular polysulfurated metallodendrimers were prepared via coordination-driven self-assembly. The structures of the newly designed polysulfurated metallodendrimers were characterized by multinuclear NMR (^{1}H and ^{31}P), mass spectrometry (CSI-TOF-MS), and elemental analysis. Moreover, the shape and size of these novel metallodendrimers were investigated with PM6 semi-empirical molecular orbital methods.

1. Introduction

Coordination-driven self-assembly[1] has proven to be a particularly powerful tool for the construction of delicate supramolecular two-dimensional (2-D) and three-dimensional (3-D) metal-containing architectures with well-defined shape and size. Metal–ligand directional bonds between two or more predesigned molecular building blocks often feature significant synthetic advantages such as few steps, fast and facile construction of the final products, and inherently self-correcting, defect-free assembly. Thus by employing coordination-driven self-assembly, a great number of well-defined 2-D and 3-D metal-containing structures have been successfully designed and constructed during the past few decades.[2] However, the most 2-D metal-containing polygons were built from simple, fairly inert building blocks that are often aliphatic or aromatic in nature. Therefore many self-assembled metallocycles are, for the most part, unfunctionalized. Recently, substantial efforts have focused on incorporating suitable functional moieties onto the resulted supramolecular complexes with the aim to the fabrication of functional artificial molecular devices.[3] For instance, an *exo-functionalization* approach has been widely utilized to prepare discrete supramolecular metal-containing assemblies functionalized with crown ether, ferrocene, and hydrophobic and hydrophilic units that have been distributed within building blocks.[4]

Dendrimers have a highly branched, three-dimensional architecture, composed of several dendritic wedges that extend outward from an internal core.[5] In the past few decades, the design and synthesis of diverse dendrimers have evolved to be one of the most important subjects within modern chemistry not only because of their aesthetically pleasing structures but also as a result of their various applications in catalysis, encapsulation and delivery, and materials science.[6] It should be noted that, since the pioneering work by Newkome and co-workers[7] and Balzani and co-workers[8] in the early 1990s, metallodendrimers[9] have received considerable attention because of their potential application in catalysis,[10] biological mimetics,[9l,11] and photo- and electrochemistry.[12] For example, we have previously reported the self-assembly of a variety of metallodendrimers with cavities of various shapes and sizes such as rhomboids, triangle, and hexagons.[4f,13] Moreover, Schalley and co-workers have synthesized a family of new metallodendritic squares from 4,4′-bipyridines functionalized with Fréchet dendrons and (dppp)-Pt(II) or Pd(II) triflate.[14] Very recently, Newkome and co-workers have reported the synthesis and photophysical properties of a series of new dendron-functionalized bis(terpyridine)-iron(II) or -cadmium(II) metallomacrocycles.[15]

During the past few decades, a new family of polysulfurated aromatic dendrimers have received considerable attention because of their unique structures and potential application in photo- and electrochemistry.[16] The investigation of these dendrons containing thiol groups opened a door to some novel and rare sulfur-containing arenes. For example, the synthesis and

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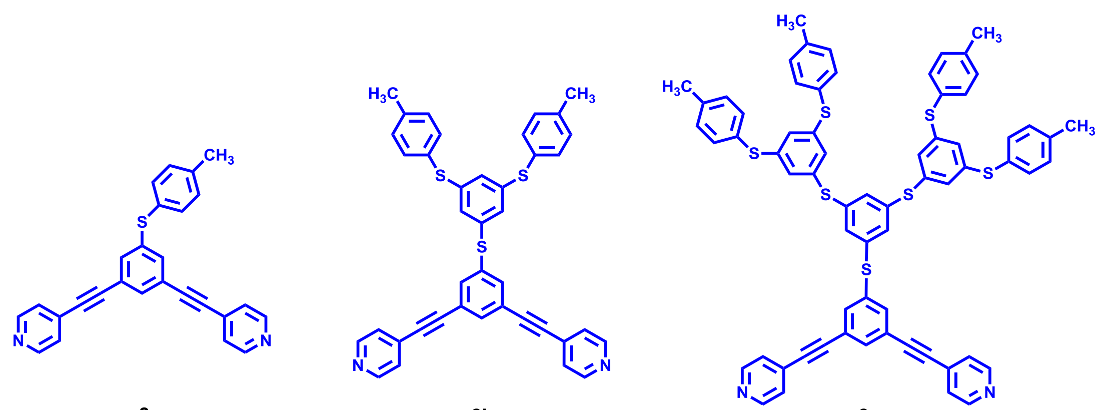
characterization of a novel class of dendrimers consisting of a polysulfurated pyrene core were presented by Gingras' group.[16a] It was found that their photophysical behavior and redox properties could be fine-tuned by the length of their branches. Moreover, a great deal of polysulfurated dendrimers with various molecular shapes such as asterisks, chains, wheels, and windmills were reported.[16b] Stimulated by our previous successful examples of supramolecular metallodendrimers,[4f,13] we envisioned that the construction of a new family of polysulfurated dendrimers with well-designed and controlled metal-containing rings would be realized by the proper choice of subunits with predefined angles and symmetry. This study could likely give rise to the design and synthesis of novel polysulfurated dendritic species with inspired functionality arising from their unique interior cavities and dendritic exteriors. Herein, we report our results on the self-assembly of polysulfurated metallodendrimers possessing rings of various size and shape at the core from newly designed [G-0]–[G-2] 120° polysulfurated dendritic donors **3a–c** (Fig. 1).

2. Results and discussion

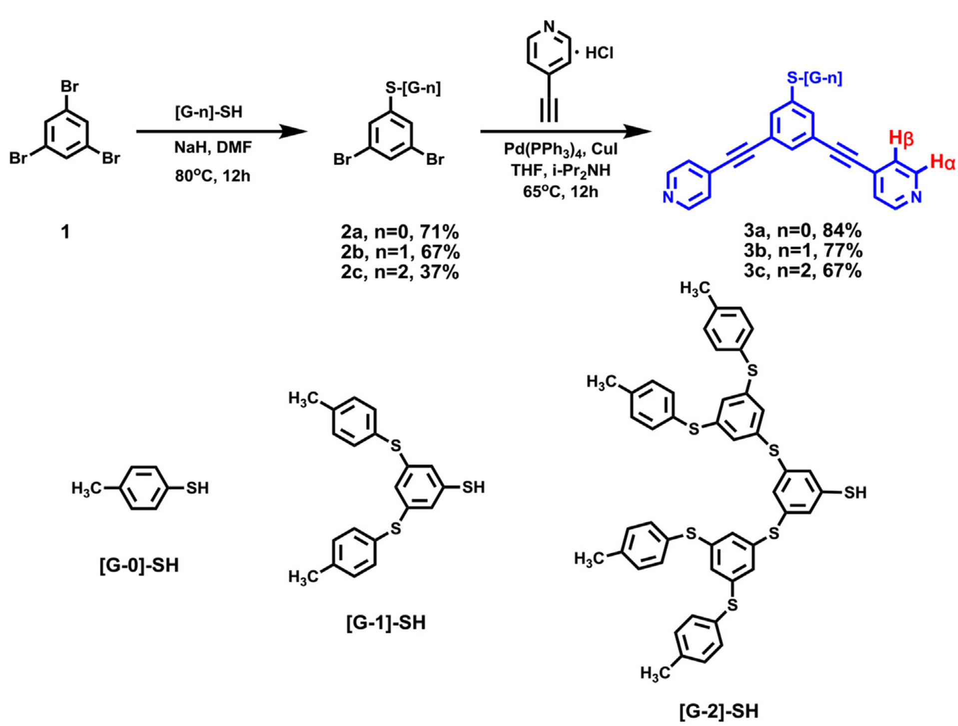
2.1. Synthesis of [G-0]–[G-2] 120° Polysulfurated Dendritic Donors 3a–c

The new 120° polysulfurated dendritic donors can be easily synthesized in two steps as shown in Scheme 1. The polysulfurated dendrimers were introduced by a nucleophilic substituting reaction of 1,3,5-tribromobenzene with the corresponding thiolate of the dendrimers.[17] The selectivity for substituting monobromide of 1,3,5-tribrotnobenzene was achieved through using a controlled amount of thiolate. From dendritic 3,5-dibromobenzene derivatives **2a–c**, the desired 120° dendritic donor building blocks **3a–c** were obtained by the coupling reaction with 4-ethynylpyridine in satisfactory yields in the presence of $Pd(PPh_3)_4$ and CuI as catalysts. The molecular structures of polysulfurated dendritic precursors **3a–c** were well characterized by using multiple nuclear NMR (^{1}H and ^{13}C) and mass spectrometry.



3a 3b 3c

Fig. 1. Molecular structures of [G-0]–[G-2] 120° polysulfurated dendritic donors **3a–c**.



Scheme 1. Synthesis of [G-0]–[G-2] 120° polysulfurated dendritic donors **3a–c**.