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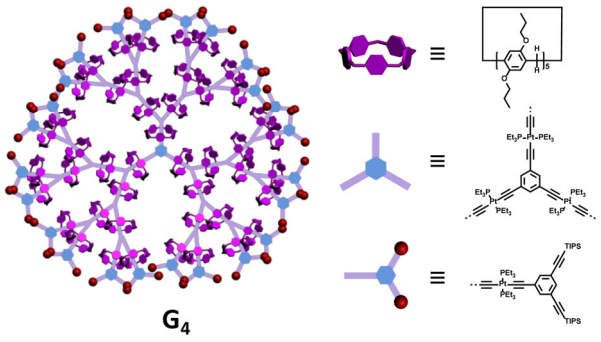
High-generation organometallic rotaxane dendrimer

Rotaxane dendrimers are a recent and novel family of mechanically interlocked dendrimers. Merging the unique characteristics of both rotaxanes and dendrimers endows the resultant rotaxane dendrimers with appealing topologic structures as well as promising properties. Thus, the design and construction of novel rotaxane dendrimers has attracted considerable attention during the past two decades [1]. However, only a very few successful examples of discrete, well-defined rotaxane dendrimers equipped with mechanically interlocked moieties on branches have been realized. Because in-depth investigations of the potential applications of rotaxane dendrimers requires the facile and efficient preparation of rotaxane dendrimers with complex and diverse structures, the development of a highly efficient synthetic strategy for producing high-generation rotaxane branched dendrimers is extremely desirable.

Very recently, a novel approach for the facile construction of high-generation branched rotaxane dendrimers has been developed by Prof. Hai-Bo Yang and coworkers from East China Normal University as reported in *Proc Natl Acad Sci USA* [2]. In their report, the host-guest complexes of the pillar[5]arene and neutral alkyl chain components were selected as the rotaxane moiety. Moreover, inspired by their sustaining investigations on platinum-acetylide complexes, the platinum-acetylide moiety was selected for use as the connecting links for dendrimer growth. According to this design strategy, a neutral organometallic rotaxane was designed and synthesized as the key building block. Starting from such precursor, a novel family of rotaxane branched dendrimers with three different types of end-groups (including triisopropylsilyl-protected and unprotected alkyne, as well as a ferrocene group) up to the fourth generation have been successfully prepared via the sequential coupling-deprotection divergent growth processes. Remarkably, in the case of the resultant fourth generation rotaxane dendrimer $\mathbf{G_4}$, 45 rotaxane moieties were mono-dispersedly distributed in the dendrimer skeleton. This is the most complex discrete multiple rotaxane system ever reported (Scheme 1). Moreover, an interesting "rotaxane effect" has been observed in such systems. The existence of the pillar[5]arene wheels could enhance the rigidity of branches as well as the resultant rotaxane dendrimers. This was proven by detailed investigation of the rotaxane dendrimers and the corresponding model dendrimers without pillar[5] arene wheels by atomic force microscopy (AFM), transmission electron microscopy (TEM), diffusion ordered spectroscopy (DOSY), and dynamic light scattering (DLS) analysis.

According to this inspiring study, the preparation of novel rotaxane dendrimers with well-defined topology structure should be feasible, thus laying the foundation for in-depth investigation of rotaxane dendrimers in dynamic supramolecular systems and materials science. Moreover, the facile surface modification may allow for the construction of functional dynamic supramolecular materials with potential uses in molecular devices, supramolecular cargos, and nanoelectronics.



Scheme 1 Schematic representation of organometallic rotaxane dendrimers $\mathbf{G_4}$ with mechanically interlocked moieties incorporated on the branches.

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2 Wang W, Chen LJ, Wang XQ, Sun B, Li X, Zhang Y, Shi J, Yu Y, Zhang L, Liu M, Yang HB. Organometallic rotaxane dendrimers with fourth-generation mechanically interlocked branches. *Proc Natl Acad Sci USA,* 2015, 112: 5597–5601