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Self-assembly using dendritic building blocks—towards controllable nanomaterials

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Abstract

Dendritic molecules have well defined, three-dimensional branched architectures, and constitute a unique nanoscale toolkit. This review focuses on examples in which individual dendritic molecules are assembled into more complex arrays via non-covalent interactions. In particular, it illustrates how the structural information programmed into the dendritic architecture controls the assembly process, and as a consequence, the properties of the supramolecular structures which are generated. Furthermore, the review emphasises how the use of non-covalent (supramolecular) interactions, provides the assembly process with reversibility, and hence a high degree of control. The review also illustrates how self-assembly offers an ideal approach for amplifying the branching of small, synthetically accessible, relatively inexpensive dendritic systems (e.g. dendrons), into highly branched complex nanoscale assemblies.

The review begins by considering the assembly of dendritic molecules to generate discrete, well-defined supramolecular assemblies. The variety of possible assembled structures is illustrated, and the ability of an assembled structure to encapsulate a templating unit is described. The ability of both organic and inorganic building blocks to direct the assembly process is discussed. The review then describes larger discrete assemblies of dendritic molecules, which do not exist as a single well-defined species, but instead exist as statistical distributions. For example, assembly around nanoparticles, the assembly of amphiphilic dendrons and the assembly of dendritic systems in the presence of DNA will all be discussed. Finally, the review examines dendritic molecules, which assemble or order themselves into extended arrays. Such systems extend beyond the nanoscale into the microscale or even the macroscale domain, exhibiting a wide range of different architectures. The ability of these assemblies to act as gel-phase or liquid crystalline materials will be considered.

Taken as a whole, this review emphasises the control and tunability that underpins the assembly of nanomaterials using dendritic building blocks, and furthermore highlights the potential future applications of these assemblies at the interfaces between chemistry, biology and materials science.

Keywords: Dendrimers; Nanotechnology; Self-assembly; Supramolecular

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1. Introduction

Self-assembly is an incredibly powerful concept in modern molecular science. The ability of carefully designed building blocks to *spontaneously assemble* into *complex nanostructures* underpins developments in a wide range of technologies—ranging from materials science through to molecular biology [1]. Self-assembly is a *supramolecular* approach which relies on complementary non-covalent interactions, such as electrostatic interactions, hydrogen bonds, van der Waals forces, coordination interactions and solvophobic effects [2]. In self-assembled structures, these temporal intermolecular forces connect the molecular scale building blocks in a *reversible*, *controllable* and *specific* way. Of particular value are the possibilities offered by self-assembly to generate nanoscale complexity with relatively *little synthetic input*. Furthermore, the ability of assembled superstructures to behave as more than the sum of their individual parts, and exhibit completely new types of behaviour, is of special interest.

Dendrimer chemistry is another key area of nanoscale science—indeed dendritic molecules can be considered to be a unique nanoscale toolkit [3a–d]. However, even though the synthesis of dendritic molecules is iterative and involves simple repetitive synthetic steps, it is still often time-consuming and tedious to generate perfect nanoscale dendritic structures. Self-assembly therefore offers an attractive option by which dendritic building blocks, many of which can be relatively small and synthetically accessible, can be simply assembled into more complex architectures. This has the effect of amplifying the dendritic branching and generating new supramolecular dendrimers (Fig. 1). There are many ways in which supramolecular chemistry can be combined with dendrimer technology (e.g. host–guest binding, etc.) and for a full discussion the reader is directed to a number of excellent reviews [4a–g], however, this article focuses on the *self-assembly of*