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Functional Molecular Nanostructures

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Contents of Volume 226
Colloid Chemistry I

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Contents

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Functional, Discrete, Nanoscale Supramolecular Assemblies

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In the schemes, several nanostructures have been depicted without unnecessary alkyl or other groups for clarity purposes.

Abstract The last decade has witnessed an unprecedented pursuit of discrete, nanoscale supramolecular aggregates, built by modern methods of self-assembly strategies. Several efficient new synthetic methods have been developed for engineering spectacular multicomponent supramolecular aggregates. Amongst all the techniques explored, metal coordination and hydrogen-bonding motifs are the most celebrated means of producing structurally rich supramolecular architectures. While a truly biomimetic approach would typically employ a balanced mixture of weak interactions (hydrogen-bonding, π-π interactions, etc.), stronger non-covalent interactions (such as the coordinative metal ligand bond) have equally proven their high utility in the preparation of nanoscale assemblies. The time has now come to install functional elements to nanoscale aggregates in order to build nanoscale devices that exhibit non-linearity, interdependence and emergence, i.e. typical characteristics of more complex systems. Currently, functional model designing is still in its early stages, and lags far behind the progress made in structural engineering. Hence, in the present article some recent advances in the structural design of nanoscale assemblies are shown, along with examples from the following areas: supramolecular catalysis, photoactive assemblies, molecular recognition and switches, and electroactive assemblies.

Keywords Nanoscale · Supramolecular · Hydrogen bond · Metal coordination · Molecular recognition · Catalysis · Photoactive aggregates (functional aggregates)

1 Introduction

For millions of years, nature has capitalised on self-assembly strategies based on non-covalent interactions, such as hydrogen bonds, salt bridges, solvation forces and even metal coordination, to organise biological systems. Hence, such forces had been exploited long before the terms "supramolecular chemistry" and "self-assembly" were introduced [1]. It is well-known that protein function largely depends on the global conformation of the protein, and the folding process is governed by a multitude of reversible non-covalent interactions [2]. The folding is guided by several elements of control, such as recognition and self-sorting, which lead the way to the desired shape (correct folding). By learning these lessons from biology, chemists are now starting to compose highly complex chemical systems from components that interact via noncovalent intermolecular forces.

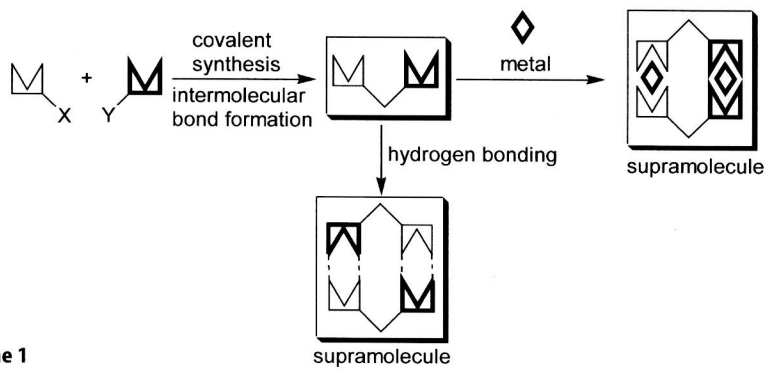
The *de novo* preparation of complex and large structures relying on covalent synthesis is often a very difficult and time-consuming chore. In contrast, supramolecular chemistry offers a convergent entrée to the creation of nanoscale systems for a wide range of applications.

The construction of nanostructures is of great interest not only because of their biological archetypes, but also because of their potential to revolutionise novel technologies such as the development of molecular-level devices. Over the last few decades, numerous supramolecular aggregates have been studied, thus revealing the principles that guide the necessary critical balance of weak interactions. As described by Lehn [1], the supramolecular architecture is a sort

of molecular sociology in which non-covalent interactions and the individual properties of the molecules define the intermolecular bond. In this article, we highlight the most often used synthetic strategies to multicomponent [3] nanoscale assemblies (>2 nm), and their chemical and physical properties in view of their potential applications as molecular devices. The vast area of inorganic and organic/inorganic cluster chemistry with strong M-M or M-ligand bonds will not be covered here, although also nanoscopic aggregates have equally been realised by such strategies [4–6].

2
Supramolecular Nanoscale Structures

The self-assembly process, driven by non-covalent interactions that are prominent in biological systems (electrostatic, hydrogen-bonding, π-π stacking, etc.), offers a great tool for engineering nanoscale structures. Using developed non-covalent protocols several groups have created sparkling architectures, such as rosette aggregates [7, 8], self-assembled capsules (for reviews see [9]), and ordered hydrogen-bonded arrays [7, 10] (Scheme 1).



Scheme 1

Formation of nanoscale supramolecular arrays was also achieved using coordination chemistry. This protocol has been adopted by several groups to yield spectacular discrete architectures, such as grids, squares, nanoboxes, ring-in-ring structures, catenanes and rotaxanes, etc., which will be discussed below.

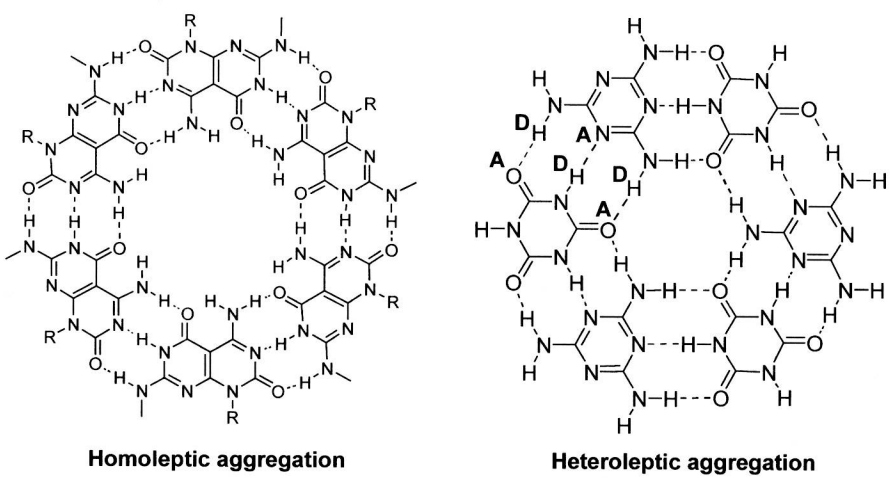
A detailed analysis of synthetic protocols leading to discrete nanoscopic self-assembled systems (>2 nm) reveals clearly that two motifs dominate the scene: hydrogen-bonding and metal-coordination-driven approaches. This review will therefore highlight some recent developments in this field, including a discussion about functional devices.

3
Hydrogen-Bond-Driven Supramolecular Nanoscale Assemblies

As indicated above, hydrogen-bonding motifs play an important role in biological systems, which adds a biomimetic flavour to all artificial hydrogen-bonded 2D and 3D assemblies. A thorough analysis of the size of known aggregates reveals that relatively few discrete hydrogen-bonded assemblies with dimensions above 2 nm, to which this article is restricted, are known.

3.1
2D and 3D Motifs

All larger (>2 nm) hydrogen-bonded assemblies are based on a multitude of hydrogen-bonding interactions in order to compensate entropic losses by enthalpic gains. Sessler et al. described the assembly of artificial dinucleotide modules to yield homoleptic 2D-scaffolds [11]. The stability of these homodimers is improved with respect to their monomer units when a rigid linker is used. A later report by the same group further illustrated the importance of structural rigidity and cooperativity [12]. Along these lines Fenniri et al. utilised heteroaromatic bases possessing both the Watson-Crick DDA pattern of guanine (where A is acceptor and D is donor) and the AAD design of cytosine to mastermind homoleptic rosette aggregates in water (Scheme 2, left). These homoleptic rosette-assemblies further aggregate into nanotubes through hierarchical self-assembly [8a]. Analogously, the ADA hydrogen-bonding arrays of isocyanuric acid are mutually complementary with DAD arrays of melamine. A detailed study of these interactions initiated the engineering of nanoscale scaffolds based on these two building blocks [13]. Hence, the combination of



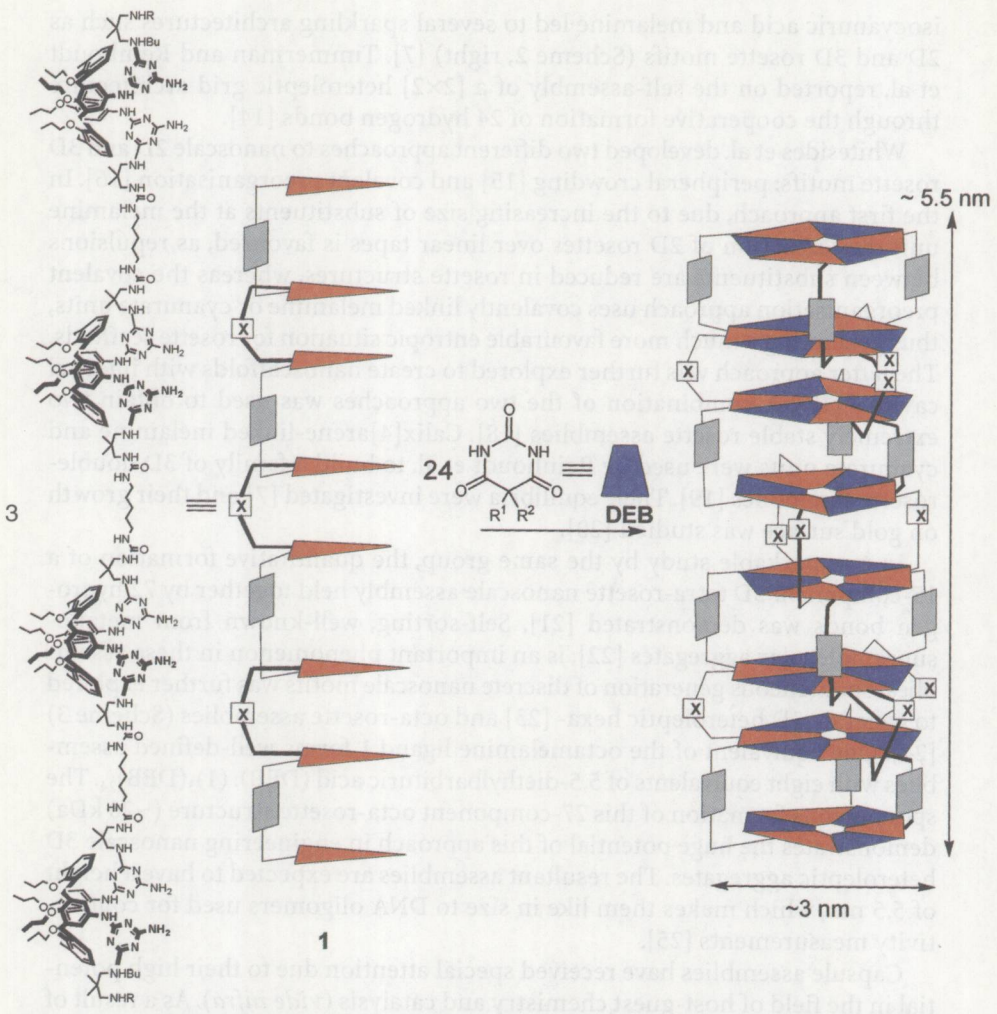
Scheme 2 Strategies used to construct homoleptic and heteroleptic 2D-rosette aggregates [7, 8a]. *A* Acceptor, ***D*** donor

isocyanuric acid and melamine led to several sparkling architectures such as 2D and 3D rosette motifs (Scheme 2, right) [7]. Timmerman and Reinhoudt et al. reported on the self-assembly of a [2×2] heteroleptic grid architecture through the cooperative formation of 24 hydrogen bonds [14].

Whitesides et al. developed two different approaches to nanoscale 2D and 3D rosette motifs: peripheral crowding [15] and covalent preorganisation [16]. In the first approach, due to the increasing size of substituents at the melamine unit the formation of 2D rosettes over linear tapes is favoured, as repulsions between substituents are reduced in rosette structures, whereas the covalent preorganisation approach uses covalently linked melamine or cyanurate units, thus generating a much more favourable entropic situation for rosette scaffolds. The latter approach was further explored to create nanoscaffolds with internal cavities [17]. A combination of the two approaches was used to obtain two extremely stable rosette assemblies [18]. Calix[4]arene-linked melamine and cyanurate units were used by Reinhoudt et al. to build a family of 3D double-rosette assemblies [19]. Their equilibria were investigated [7] and their growth on gold surface was studied [20].

In a remarkable study by the same group, the quantitative formation of a 15-component 3D tetra-rosette nanoscale assembly held together by 72 hydrogen bonds was demonstrated [21]. Self-sorting, well-known from metallo-supramolecular aggregates [22], is an important phenomenon in these assemblies. Spontaneous generation of discrete nanoscale motifs was further explored to generate 3D heteroleptic hexa- [23] and octa-rosette assemblies (Scheme 3) [24]. One equivalent of the octamelamine ligand **1** forms well-defined assemblies with eight equivalents of 5,5-diethylbarbituric acid (DEB): $(\mathbf{1})_3(\mathrm{DEB})_{24}$. The spontaneous formation of this 27-component octa-rosette structure (~20 kDa) demonstrates the huge potential of this approach in engineering nanoscale 3D heteroleptic aggregates. The resultant assemblies are expected to have a height of 5.5 nm, which makes them like in size to DNA oligomers used for conductivity measurements [25].

Capsule assemblies have received special attention due to their high potential in the field of host-guest chemistry and catalysis (*vide infra*). As a result of the difficulties in constructing capsules by covalent synthesis [26] several groups have explored the fabrication of capsules relying on non-covalent synthesis. Most of the self-assembled capsules reported to date are homoleptic in nature [9a,c, 27] with only a couple of heteroleptic capsules being known. As shown in Fig. 1, six strategies to achieve capsule-like assemblies are explored [7]. While calix[4]arenes, resorcinarenes and cavitands are amongst the most extensively used building blocks, homoleptic capsule formation from calix[4]arenes is hampered due to its high conformational flexibility. Calix[4]arenes, with four urea moieties at the upper rim that allow for sideway-directed urea hydrogen bonds, form well-defined homoleptic capsules in solution (Fig. 1d) [28]. A similar strategy was used to construct homodimers from cyclocholates [29], cyclotriveratrylenes [30] and a heterodimer from complementary cyclodextrin and porphyrin moieties [31]. Rebek et al. prepared homoleptic capsules of



Scheme 3 Hydrogen bond self-assembly of 27 components leading to a heteroleptic rosette aggregate [24]. *DEB* 5,5-Diethylbarbituric acid

tennis ball shape using the hydrogen-bonding properties of glycoluril moieties (Fig. 1b and f) [32]. A similar strategy was explored to construct capsules using glycoluril and sulphamides as complementary hydrogen-bonding blocks (Fig. 1a) and self-assembly of the tetramide block (Fig. 1c). For heteroleptic hydrogen-bonded capsules, the versatile approach (Fig. 1d) was used by Reinhoudt et al. [33], Rebek et al. [34] and others [35]. To construct heteroleptic capsules, two cavitands with carboxylic acid groups serve as end-caps and four 2-aminopyridine molecules act as connectors [36]. These heteroleptic capsules are of particular interest because one can readily introduce multiple functionalities. All these capsules range from ~2 to 3 nm in size.

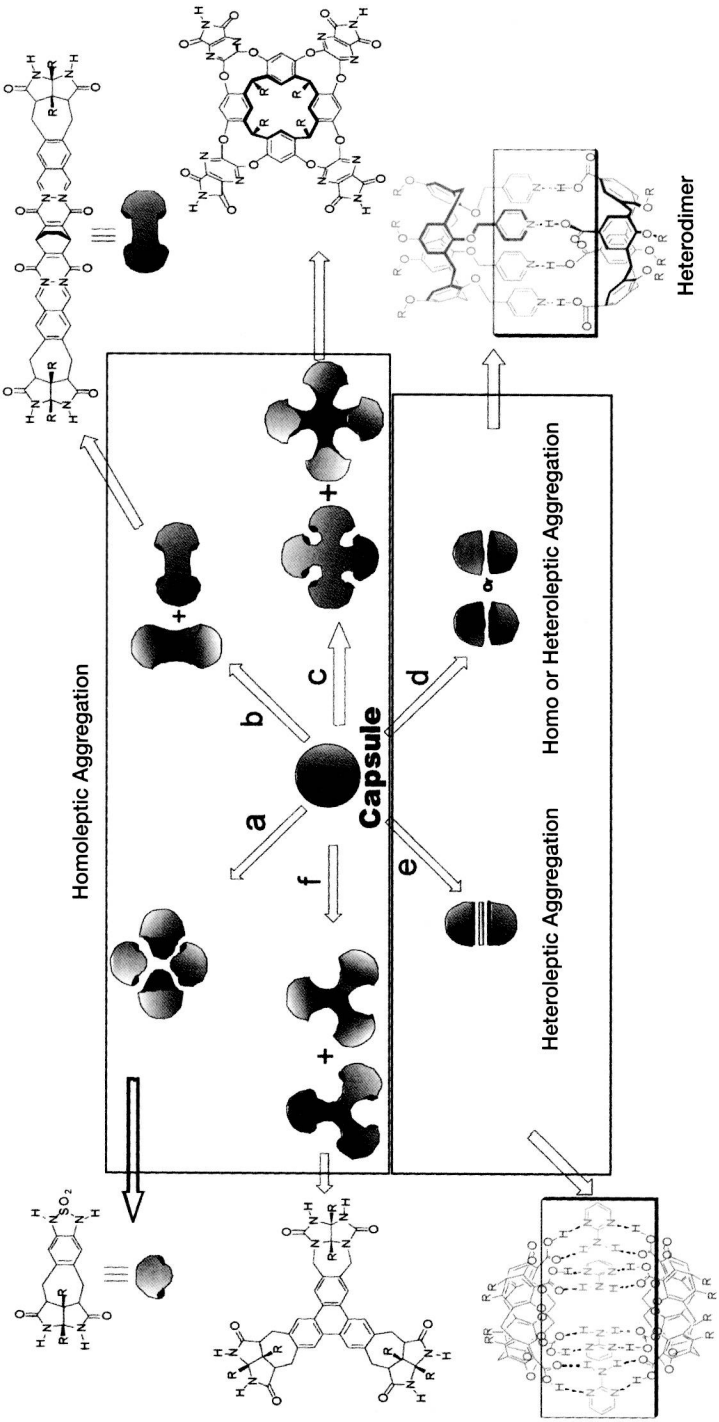
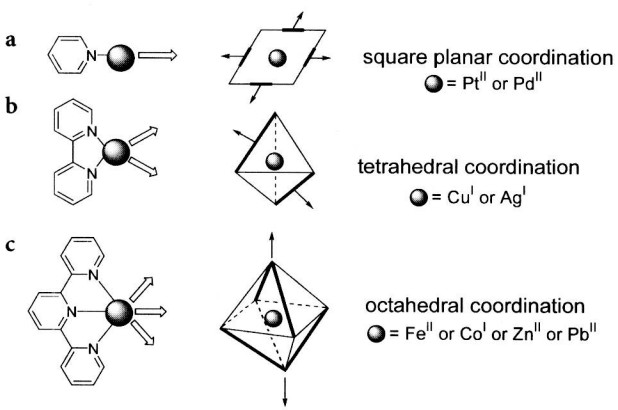


Fig. 1 Strategies used to construct homo and heteroleptic capsule like nanoscale assemblies [28–36]

4
Coordination-Driven Supramolecular Nanoscale Assemblies

4.1
Design

The metal coordination geometry and the information stored in the ligands should provide the construction manual for any self-assembly. Therefore, the selection of appropriate metal ion(s) and ligand(s) is crucial, as witnessed in a multitude of publications, reviews, and books. In this chapter, we will concentrate on nanoscale architectures built from monodentate (pyridine), bidentate (bipyridine, phenanthroline, catechol) and tridentate (terpyridines) ligands. The dentate term is here used purely to describe the interaction of the ligand with one single coordination centre. As depicted in a simplified way in Scheme 4, most self-assemblies described in the literature are constructed about Pd(II) or Pt(II) ions in a square planar arrangement using monodentate ligands, at Cu(I) or Ag(I) ions in a tetrahedral fashion making use of bidentate ligands, and at Co(II)/Cu(II)/Fe(II)/Zn(II)/Hg(II) in an octahedral grouping by employing terpyridine chelating motifs.



Scheme 4a–c Cartoon representation of preferred coordination geometry of **a** monodentate, **b** bidentate, and **c** tridentate ligands

4.2
Nanoscale Self-Assemblies Built Using Monodentate Ligands

Stang et al. [37], Fujita et al. [38] and Hupp et al. [39] have shown the utility of monodentate ligands in developing nanoscale supramolecular architectures. As emphasised by Stang et al. [37a], the important factors to be considered are the coordination angles at the metal ion equipped with a kinetically inert ligand and at the incoming labile multitopic ligand. This design is usually termed the