

ADVANCES IN
SUPRAMOLECULAR CHEMISTRY

Edited by GEORGE W. GOKEL

Volume 6

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PREFACE

It has long been the goal of *Advances in Supramolecular Chemistry* to present a broad range of supramolecular science rather than to organize a focused volume. Monographs dedicated to a single subject have great and obvious value but they are inherently narrow. As the field of supramolecular chemistry has grown, a number of useful, focused monographs have appeared. Those desiring an up-to-date assessment of a particular area will clearly benefit from such volumes. In contrast, the intent in this series has always been to present an overview of scientific endeavors in the broad discipline called supramolecular chemistry that spans analytical, inorganic, organic, physical, and biochemistry.

In Volume 6 of the series, inorganic, organic, and bioorganic chemistry are represented in contributions from Germany, Japan, Korea, Switzerland, the United States, and The Netherlands. In the first chapter, Biradha and Fujita describe their pioneering work in self-assembled structures organized by the use of transition metals. Feiters and Nolte then describe their extensive studies of self-assembled structures formed from various biomolecules. MacGillivray and Atwood describe the formation of spherical molecular containers and their understanding of such structures based on Platonic and Archimedean solids. Schneider, Eblinger, and Sirish describe the fascinating family of synthetic peptide receptors and the interactions that can be explored using these host molecules. In the next chapter, Riley describes a mixture of computational chemistry, drug design, and synthetic organic and inorganic chemistry in the development of superoxide dismutase mimics. Suh

discusses the bioorganic and supramolecular principles required for the design of synthetic artificial enzymes. In the final chapter, Luisi discusses supramolecular self-assembly and its possible role in the origin of life.

It is hoped that this broad, international view of supramolecular chemistry and the many directions it leads will be of interest to those already in the field. It is also hoped that those outside the field may see extensions of their own work that will bring them into it.

G. W. Gokel
Editor

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1 Introduction to Block Copolymers

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1.1 INTRODUCTION

Block copolymers are useful in many applications where a number of different polymers are connected together to yield a material with hybrid properties. For example, thermoplastic elastomers are block copolymers containing a rubbery matrix (polybutadiene or polyisoprene) containing glassy hard domains (often polystyrene). The block copolymer, a kind of polymer alloy, behaves as a rubber at ambient conditions, but can be moulded at high temperatures due to the presence of the glassy domains that act as physical crosslinks. In solution, attachment of a water soluble polymer to an insoluble polymer leads to the formation of micelles in amphiphilic block copolymers. The presence of micelles leads to structural and flow characteristics of the polymer in solution that differ from either parent polymer.

A block copolymer molecule contains two or more polymer chains attached at their ends. Linear block copolymers comprise two or more polymer chains in sequence, whereas a starblock copolymer comprises more than two linear block copolymers attached at a common branch point. Polymers containing at least three homopolymers attached at a common branching point have been termed mixed arm block copolymers, although they can also be viewed as multigraft copolymers.

In the following, block copolymers prepared by controlled polymerization methods only are considered, primarily di- and tri-block copolymers (see Figure 1.1). Multiblock copolymers such as polyurethanes and poly (urethane-ureas) prepared by condensation polymerisation are not discussed. Whilst these materials do exhibit microphase separation, it is only short range in spatial extent due to the high polydispersity of the polymers.

A standard notation for block copolymers is becoming accepted, whereby X-*b*-Y denotes a diblock copolymer of polymer X and polymer Y. However, sometimes the *b* is replaced by the full term *block*, or alternatively is omitted, and the diblock is denoted X-Y.

A number of texts covering general aspects of block copolymer science and engineering appeared in the 1970s and 1980s and these are listed elsewhere [1]. More recently, specialised reviews have appeared on block copolymer melts and

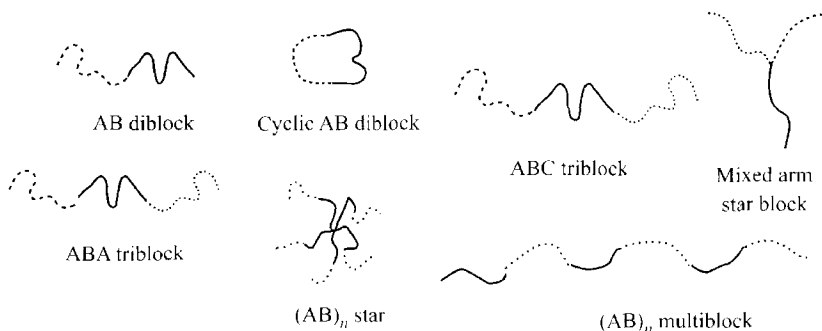


Figure 1.1 Block copolymer architectures.

block copolymer solutions, and these are cited in Sections 1.3 and 1.4 below. The burgeoning interest in block copolymers is illustrated by contributions covering various aspects of the subject in a review journal [2] and in a book [3].

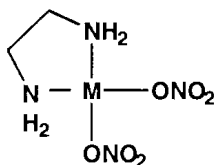
Since the excellent review by Riess *et al.* [4] there have been many advances in the field of block copolymer science and engineering, including new synthesis methods, developments in the understanding of phase behaviour and the investigation of structure and dynamics in thin films. Many of these advances are likely to lead soon to novel applications.

1.2 SYNTHESIS

The main techniques for synthesis of block copolymers in research labs around the world are presently anionic polymerization and controlled radical polymerization methods. The older technique of anionic polymerization is still used widely in the industrial manufacture of block copolymers. Cationic polymerization may be used to polymerize monomers that cannot be polymerized anionically, although it is used for only a limited range of monomers. A summary of block copolymer synthesis techniques has been provided by Hillmyer [5].

1.2.1 ANIONIC POLYMERIZATION

Anionic polymerization is a well-established method for the synthesis of tailored block copolymers. The first anionic polymerizations of block copolymers were conducted as early as 1956 [6]. To prepare well-defined polymers, the technique is demanding, requiring high-purity starting reagents and the use of high-vacuum procedures to prevent accidental termination due to the presence of impurities. In the lab, it is possible to achieve polydispersities $M_w/M_n < 1.05$ via anionic polymerization. The method is also used industrially to prepare



1

a: M = Pd; b: M = Pt

without losing the Pd(en)/Pt(en) framework because of the dissociation of en ligand from the metal is negligible under ordinary conditions, whereas monodentate ligands undergo rapid dissociation. Based on such an idea, novel *cis*-protected Pd(II) and Pt(II) building blocks **1a** and **1b** were designed. These metal building blocks have shown a remarkable ability in inducing a self-assembly process. This review focuses on our efforts in designing self-assemblies of a variety of discrete architectures using **1a** or **1b** and several pyridine-based ligands. The designed architectures include squares, macrocycles, catenanes, cages, and tubes. Most of these self-assemblies were shown to be stable both in solution and solid and are characterized by proton nuclear magnetic resonance (^1H NMR), electron spray mass spectroscopy (ESI-MS),¹⁶ and X-ray crystallography.

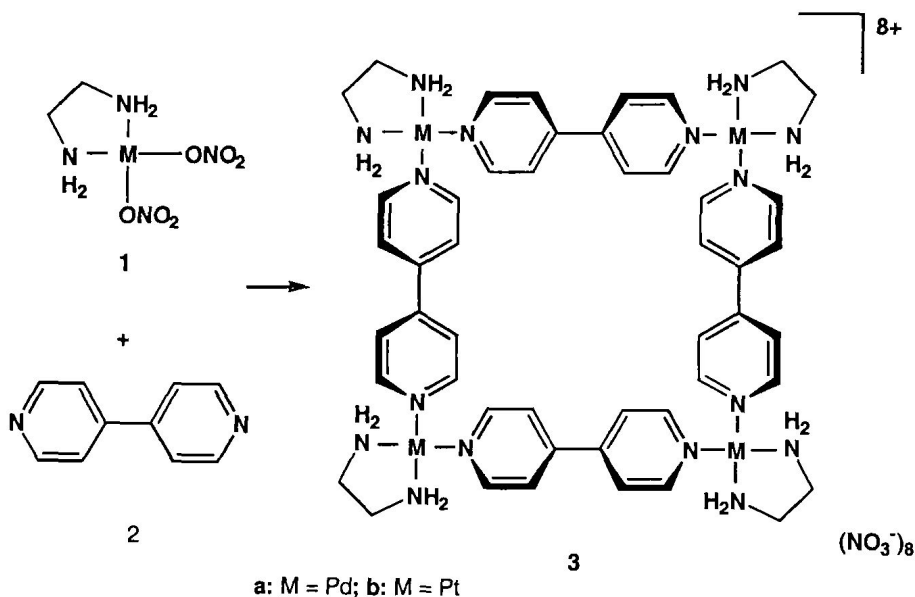
2. SELF-ASSEMBLING TETRANUCLEAR Pd(II) MACROCYCLE

2.1. Pd(II)-(4,4'-bipy) Square Complexes

The linear bifunctional and exodentate nature of 4,4'-bipyridine, **2**, and 90° coordination angle of **1a** were used in combination to design a square complex, **3a**.¹⁷ It was synthesized in quantitative yield by simply mixing **1a** and **2** in 1:1 ratio in water (Scheme 1). This compound is the first example of molecular squares which have attracted considerable current interest.¹⁸ The solution structure was confirmed using NMR and ESI-MS, whereas the solid-state structure was determined by X-ray crystallography.¹⁹ The crystal structure of **3a** revealed an almost perfect square structure with facial conformation of pyridine nuclei (Figure 1).

The square cavity in **3a** is of dimension ca. $8 \times 8 \text{ \AA}$ and offers encapsulation of variety of aromatic guest molecules because of its hydrophobic nature. Thus, we found the ability of **3a** to recognize several neutral aromatic molecules from water (Table 1).²⁰ For example, 1,3,5-trimethoxybenzene was recognized with K_a value of 7.5×10^2 .

The square structure **3a** was expanded further by simply inserting spacers such as *p*-phenylene, $-\text{C}\equiv\text{C}-$ or $-\text{C}=\text{C}-$ units between the pyridine units of **2**. Interestingly in expanded structures, the molecular square **4** was in equilibrium with the

*Scheme 1.*

trinuclear triangle, **5**, depending on the concentration of the components (Scheme 2).¹⁹ Hong and coworkers reported recently that this equilibrium can be controlled by guest-induced molecular recognition.²¹ That is, the small guest molecules shifted the equilibrium towards molecular triangle **5b**, whereas the large guest molecules shifted the equilibrium towards molecular square **4b**.

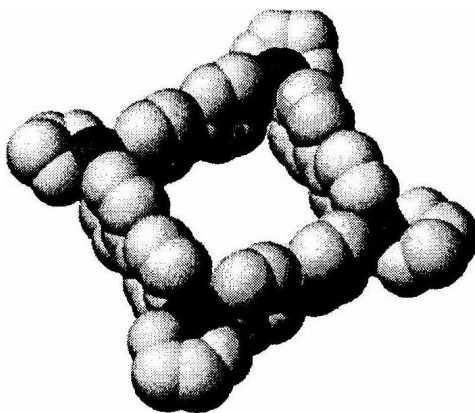
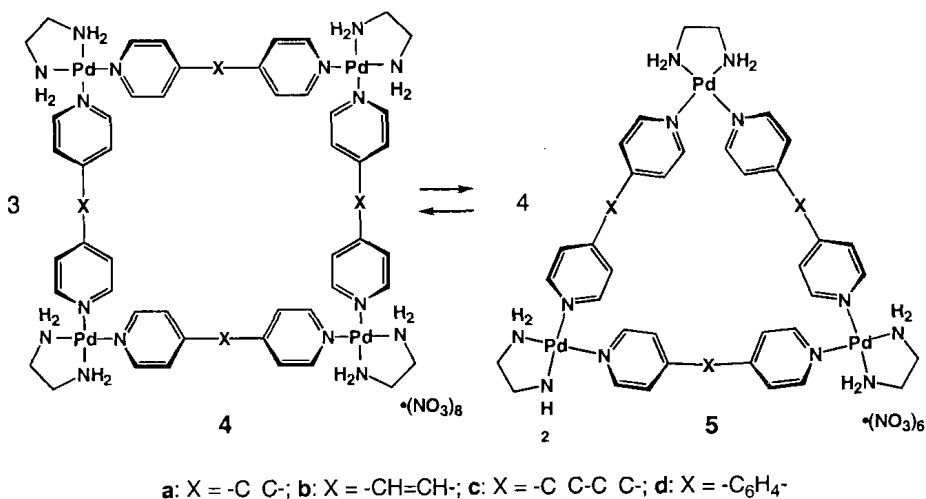
*Figure 1.* The molecular square in the crystal structure of **3a**.

Table 1. Association Constants for the Various Self-Assembled Macrocycles and Guests

Host	Guest	Association Constant (L mol ⁻¹)	Ref.
3a	N-(2-naphthyl)acetamide	1800	25
	1,3,5-trimethoxybenzene	750	17
	p-dimethoxybenzene	330	20
	m-dimethoxybenzene	580	20
	o-dimethoxybenzene	30	20
	p-bis(methoxymethyl)benzene	10	20
	1,4-dimethoxycyclohexane	n.c.	20
3b	p-dimethoxybenzene	260	20
	m-dimethoxybenzene	550	20
	o-dimethoxybenzene	20	20
4b	1,3,5-trimethoxybenzene	420	a
	p-dimethoxybenzene	130	a
13	p-dimethoxybenzene	200	37
	p-dicyanobenzene	201	37
	14	1,3,5-trimethoxybenzene	2500
p-dimethoxybenzene		2580	25
p-bis(methoxymethyl)benzene		560	25
p-dicyanobenzene		80	25
p-dinitrobenzene		30	25

Note: ^aUnpublished results.



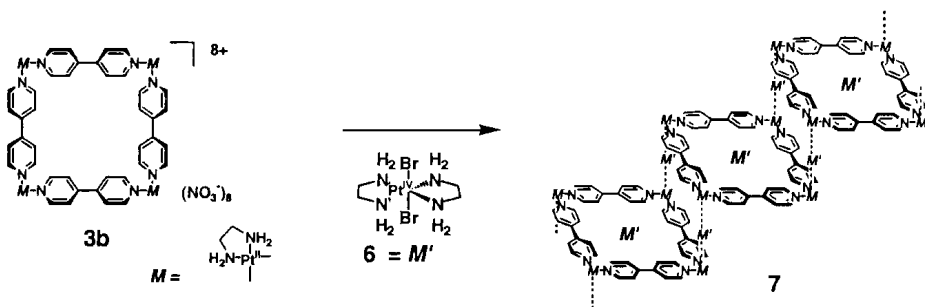
Scheme 2.

2.2. Stability of Square Complexes

The self-assembly of Pt(II) analogue **1b** with **2** was very slow due to the inactivity of the Pt(II)–pyridine bond. Thus, upon treatment of **1b** with **2**, a kinetically distributed oligomeric mixture was initially formed.²² However, the mixture gradually turned into the thermodynamically most stable molecular square **3b** after heating the solution for a few weeks at 100 °C. The use of bis-nitrate salt of **2**, instead of **2** itself, dramatically increased the reaction rate as well as the yield (79–81%). Similar improvements in reaction rate and yield were observed by the addition of NaNO₃ to the reaction. A significant difference in stability was found between **3a** and **3b**. The addition of **1a** to **3a** in D₂O resulted in dissociation of **3a** to give a mixture of **3a** (ca. 50%) and two acyclic components which have **1a** and **2** in 1:2 and 2:3 ratios. In a striking contrast, **3b** remained intact even upon the addition of **1b**, as its structure had been locked by the inert Pt–Py bond. The square complex **3b** was also found to show inclusion properties similar to **3a** (Table 1).

2.3. Accumulation of Pd₄ Square Complexes

The square compounds **3a** and **3b** were used as building blocks to construct a one-dimensional staircase and tubular networks by bridging the corners of the squares with X–Pt–X (X = Cl, Br) units.²³ We anticipated these architectures in the mixed valence complexes which can be easily synthesized by simply mixing two metal complexes that have different valences.²⁴ Accordingly, the molecular square **3b** was prepared and then mixed with [Pt(en)₂Br₂]Cl₂ (**6**) in an aqueous solution of NaNO₃ (Scheme 3). The single crystals of 1:3 complex **7** of **3b** and **6** were obtained and characterized by X-ray crystallography. The crystal structure shows one square moiety, **3b**, and two moieties of **6** form a staircase like network, while the third moiety of **6** acts as a guest molecule and occupies in the square cavity of **3b** (Figure 2). The Pt(II)–Br distance in **7** (3.22 and 3.37 Å) indicates a weak interaction between Pt(II) and the Br atom. The geometry of the square in **7** is similar to that of the above-described square complex **3b**. It is interesting to note that a cationic



Scheme 3.

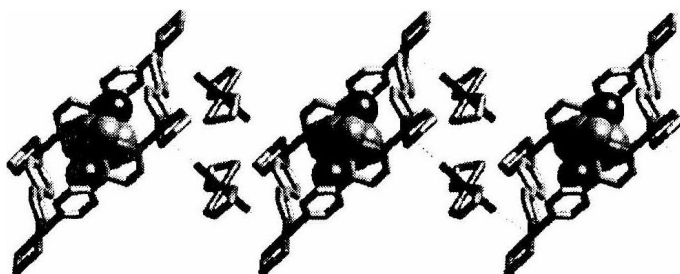
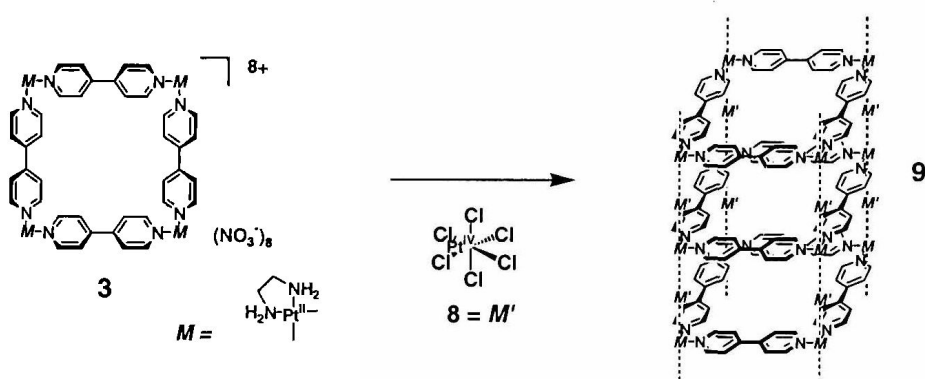


Figure 2. Staircase network in the crystal structure of **7**. Note that one moiety of **6**, represented in space filling mode, occupied in the scare cavity of **3b**.

species **6** was encapsulated by a cationic square **3b** because of the perfect match of their shape and size. It indicates that an unfavorable electrostatic effect was overridden by a favorable shape factor.

Similarly, the accumulation of the squares **3a** or **3b** were also observed via anionic complex $[\text{PtCl}_4]^{2-}$ (**8**). The formation of complex $(\mathbf{3a}.\mathbf{8})_4$ in 94% yield was observed when the aqueous solutions of **3** and **8** were combined at any given ratio (Scheme 4). The product was characterized by UV-vis and elemental analysis. The UV-vis shows new absorption peaks at 390 and 490 nm, which indicates the existence of an interaction between Pd(II) and Pt(IV). The elemental analysis of the complex confirms ratio of **3a** and **8** is 1:4. These observations suggest that the structure of this complex could be a polytube **9** in which each corner of the square is linearly bridged by the linear Br–Pt–Br motif. It seems logical that the accumulation of the cationic squares with anionic species leads to a tubular network rather a staircase network because of favorable electronic effects.



Scheme 4.

3. SELF-ASSEMBLING MACROCYCLES

3.1. Structure and Molecular Recognition

In the previous section we have shown that the rigid bifunctional ligands can form molecular squares or triangles. Here we show that the flexible bidentate ligands can form binuclear macrocycles and discuss their ability towards the inclusion of guest molecules.

The macrocycles **10–18** were prepared in quantitative yields by simply mixing the corresponding ligands and **1a** in 1:1 ratio in water.^{25–28} Structures **10**, **12**, **17**, and **18** were fully characterized by X-ray crystallography (Figure 3) and the other structures were characterized by fast atom bombardment mass spectrometry (FABMS). The guest inclusion properties of these macrocycles were studied using ¹H NMR. It is interesting to note that some of them showed a unique ability for molecular recognition. For example, macrocycle **14** having two tetrafluorophenylene units exhibited a remarkable molecular recognition ability for electron-rich aromatic compounds. Thus, the association constants increased with increasing electron density of the guest molecules (see Table 1). The inclusion geometry of these macrocycles was suggested from the crystal structure of the related infinite Cd complex $\{[\text{Cd}(\mu\text{-}\mathbf{13})_2](\text{NO}_3)_2 \cdot (p\text{-NH}_2\text{C}_6\text{H}_4\text{NO}_2)\}_n$, **19**, in which the macrocyclic framework of **13** repeats one-dimensionally (Figure 4).²⁹ Efficient edge-face aromatic interactions in the cavity are probably a driving force for high efficient molecular recognition.

3.2. M_6L_4 Macrotricyclic Complexes

Here we discuss the formation of macrotricycles by exotridentate ligands and also discuss their remarkable ability to bind dicarboxylates. Treatment of the Pd(II) complex, **1a**, with the ligands **20** and **21** resulted in the self-assembly of macrotricyclic frameworks **22** and **23**, respectively (Scheme 5).³⁰ The formation of **22** and **23** were characterized in solution by ¹H NMR and in the solid state by X-ray crystallography (Figure 5). Further, the addition of NaClO₄ to the aqueous solution of **22** or **23** resulted in the precipitation of corresponding ClO₄ salts in 85% yield. These frameworks were held together by 10 molecular components (six metal ions and four ligands) and the most significant feature is that they have nanometer dimensions in spite of the small size of the molecular components. The X-ray structures show **22** and **23** have molecular dimensions of ca. 30 × 23 × 22 Å and 27 × 24 × 14 Å, respectively, and have the same topologies. Although they have same topologies, their cavity shapes differ significantly: **22** has an elliptical cavity, while **23** has a bowl shape cavity.

The proposed pathway leading to formation of **22** or **23** involves a two-step self-assembly process; that is via the formation of intermediates, **24** and **25** for **22** and **23**, respectively. The first step is the formation of **24** and **25**, whereas the second step is self-assembly of **24** and **25**. This pathway was supported by the isolation of