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1,3,5-Triazine-Based Synthons in Supramolecular Chemistry

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Interest in supramolecular chemistry has grown significantly during the past two decades. In this context, hydrogen bonding and/or coordinative interactions have been extensively used to generate self-assembled one-, two- or three-dimensional polymeric networks. Crystal structure prediction has progressed tremendously, and the challenge for the contemporary supramolecular chemist is now to produce custom-made functional (and multifunctional) materials involving intermolecular interactions. Since the early 1990s, 1,3,5-triazine derivatives have shown their potential as building blocks for the preparation of such materials. In this microreview, a selection of outstanding examples of supramolecular networks involving the 1,3,5-triazine unit are discussed, illustrating the possibility of forming remarkable architectures by means of coordination and/or hydrogen bonds and their applications in host–guest chemistry, catalysis, anion recognition, sensoring, electronics and magnetism.

1. Introduction

Supramolecular chemistry is one of the topical fields of contemporary chemistry and has first been defined in 1978 by Jean-Marie Lehn as the "chemistry of molecular assemblies and of the intermolecular bond".[1] Supramolecular chemistry is a vast interdisciplinary field of research and technology, where noncovalent bonding may be a common ground. A rapidly developing branch of supramolecular chemistry is crystal engineering, in which synthetic control is particularly required.[2,3] Nowadays, the main focus of crystal engineering is the design and synthesis of molecular building blocks whose intermolecular interactions[4] with other synthons would allow some degree of predictability regarding the form and/or function of the resulting materials.[5] For instance, the chemistry of hybrid nanostructured organic–inorganic solids involving metal–ligand coordination units is emerging as a primary research area,[6] since it offers the possibility of combining different properties at the molecular level and leading to new composite materials with unprecedented behaviour.[7,8] Furthermore, the combination of coordination chemistry with noncovalent contacts, such as hydrogen bonding[9,10] or π-interactions,[11,12] provides a powerful method for generating supramolecular networks from simple building blocks. These three types of bond are indeed important in conceiving unique frameworks, since they all involve directional interactions.[13] From the perspective of crystal engineering, the benefit of using transition-metal ions is that the shape of the coordination building unit can be controlled by choosing the coordination geometries of the metal ions properly. A more specific geometry can then be obtained by judiciously attaching suitable functional substituents to the ligands, which will act as intra- and/or intermolecular connectors. Thus inorganic–organic hybrid supramolecular assemblies with unusual network topologies should be accessible through noncovalent interactions,[14] i.e. H-bonding and π-interactions.

1,3,5-Triazine derivatives have proven their great potential in this rising area of material chemistry, both for their π-interaction abilities,[15] and for their aptitude to be involved in intricate H-bond networks.[16]

The present review deals with the background on supramolecular architectures involving the 1,3,5-triazine ring as the central building moiety. A number of triazine-containing molecules have been used in crystal engineering and have allowed outstanding new developments in the arena of tailored functional materials.[17]

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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2. Preparation of 1,3,5-Triazine-Based Organic Building Blocks

1,3,5-Triazine-containing compounds have found a number of applications in medicinal chemistry,[18] herbicides,[19] catalysis[20] or polymer chemistry.[21] Sophisticated *s*-triazine derivatives can be easily prepared from the cheap, readily available cyanuric chloride, i.e. 2,4,6-trichloro-1,3,5-triazine.[22] Cyanuric chloride is definitely an excellent synthon for the straightforward preparation of highly structured multitopic molecules.[23] Indeed, each chloride atom of 2,4,6-trichloro-1,3,5-triazine can be substituted by any nucleophile (Figure 1). The first substitution is exothermic and so the reaction mixture must be cooled down to 0 °C. The second chloride substitution can be performed at room temperature. Finally, the third position is functionalized under solvent reflux.

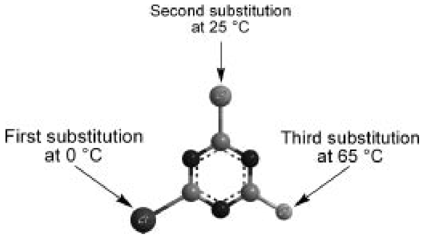


Figure 1. Differential reactivity of 2,4,6-trichloro-1,3,5-triazine.[23]

Therefore, by carefully controlling the temperature, 2,4,6-trisubstituted triazines can be synthesized by sequential, very selective addition of all kinds of nucleophiles, namely amines, alcohols, thiols or Grignard reagents (Figure 2). The yield of each substitution often exceeds 95% and the symmetric trisubstituted derivatives can even be obtained in a one pot synthesis. Various solvents can be used such as tetrahydrofuran, 1,2-dimethoxy ethane, acetonitrile, diethyl ether, and so on.

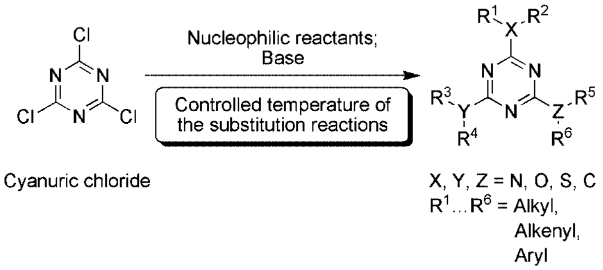
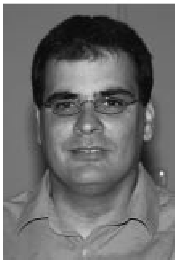


Figure 2. Preparation of polyfunctional triazine derivatives.

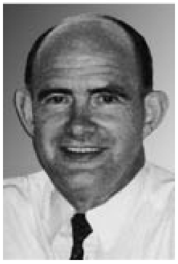
Numerous triazine derivatives have been prepared following this versatile synthetic pathway.[24–27]

3. Melamine Derivatives as Synthons for the Preparation of H-Bonded Self-Assemblies

Hydrogen bonds play a fundamental role in nature where they are particularly responsible for controlling the structure and function of many proteins, recognition of substrates by various enzymes and for the double-helix struc-



Patrick Gamez (1967, Casablanca, Morocco) studied Chemistry at the University of Lyon in France where he obtained his first degree. In 1995, he received his D. Phil. in the field of enantioselective catalysis under the supervision of Professor M. Lemaire and was awarded the French Chemical Society Prize for his PhD research. After a period of postdoctoral research at the Max-Planck-Institut für Kohlenforschung in the group of Professor A. Fürstner and at the University of Strasbourg in the group of Dr C. Mioskowski, he joined the research group of Professor J. Reedijk. His current research interests are copper biomimetics and oxidation catalysis, and design of multidentate ligands for crystal engineering. He is (co)author of about 70 publications.



Jan Reedijk was born in 1943 in The Netherlands. He is currently Professor of Chemistry at the Leiden Institute of Chemistry, Leiden University, The Netherlands. After obtaining his PhD from Leiden University in 1968 (Thesis title: Methyl Cyanide as a Ligand) and a junior lectureship, he lectured in Delft University of Technology until November 1979, when he accepted his present position. During 1993 he was a visiting Professor at Cambridge University (UK), and during 2002 at the University of Louvain-la-Neuve (Belgium). His current research interests include coordination chemistry of transition-metal ions, bioinorganic chemistry (active-site structure and mechanism; models; metal–DNA interactions), applications of coordination chemistry in catalysis, medicine, ion-exchange and surface chemistry, extended (magnetic, electric) interactions in coordination compounds (dimers, clusters, chains), and molecular recognition and intermolecular interactions (catalysis, biomacromolecules). He has over 900 (co)-authored refereed research publications and patents and has supervised over 100 postdoctoral and graduate students (since 1973). Some of his major professional activities, honours and awards are: Director Leiden Institute of Chemistry (1993–2004); Member of the International Advisory Board of a number of International Conference Organisations, such as the EURASIA Conferences of Chemistry, Macromolecular Metal Complexes Conferences, EUROBIC and ICBIC. Other honours: elected as Executive Secretary of the International Coordination Chemistry Conferences (1989) and acted as President of the Royal Netherlands Chemical Society in 1990; Board member of the Chemistry Research Council (1998–2002); Elected Honorary member of the Royal Netherlands Chemical Society; Awardee of the Max Planck Research Award in Chemistry in 1992; Elected Member of the Finnish Academy of Sciences (1997); Elected Member of the Royal Netherlands Academy of Sciences (1996); Elected Member of the Academia Europaea (2004). He is and has been a member of the editorial boards of over 15 major chemistry journals, such as: Chem. Commun., Inorg. Chem., J. Chem. Soc., Dalton Trans., New J. Chem., Russian J. Coord. Chem., J. Inorg. Biochem. and the J. Biol. Inorg. Chem. He has served on several IUPAC committees on nomenclature of (bio)inorganic, biochemical, physical organic chemistry and terminology between 1978 and 1998. He is one of the founding editors of Eur. J. Inorg. Chem. (a merger from several European Chemical Society Journals).

ture of DNA (Figure 3). Consequently, hydrogen bonding has become one of the most important noncovalent interactions in supramolecular chemistry.[28,29]

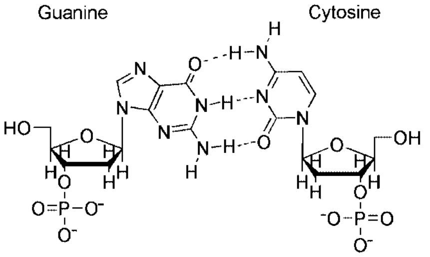


Figure 3. Watson–Crick base pairing in DNA.

Fifteen years ago, Whitesides and coworkers have shown that melamine derivatives could be used to generate outstanding aggregates.[30,31] The reaction of cyanuric acid (CA) with melamine (M) leads to the formation of an insoluble very stable (it can be heated to 450 °C without any alteration of the structure) H-bonded 2D network (Figure 4, CA•M),[30] which has been first reported in 1979 by Junichi and coworkers.[32]

In the earlier 1990s, Whitesides and coworkers have improved the preparation of this type of self-assemblies by using both substituted melamines and barbituric acids.[31] In that way, it is possible to control, by steric hindrance, the formation of the 2D frameworks. Reaction of 5,5-diethylbarbituric acid with 2-amino-4,6-(*N*-*p*-tolylamino)-1,3,5-triazine yields a linear tape (Figure 5a). If 2-amino-4,6-(*N*-*p*-methylbenzoatoamino)-1,3,5-triazine is combined with 5,5-diethylbarbituric acid, a crinkled tape is obtained (Figure 5b). Finally, with a bulkier group on the phenyl ring, i.e. *tert*-butyl, a rosette motif is achieved (Figure 5c).

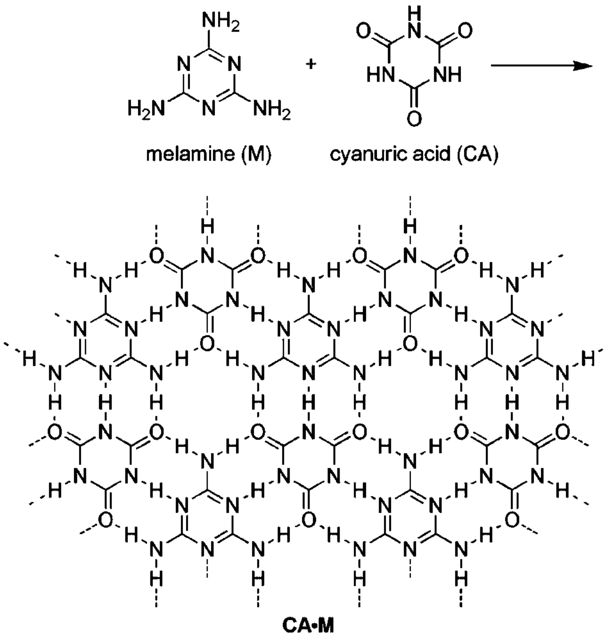


Figure 4. Self-assembly network by means of hydrogen bonds.[16,32]

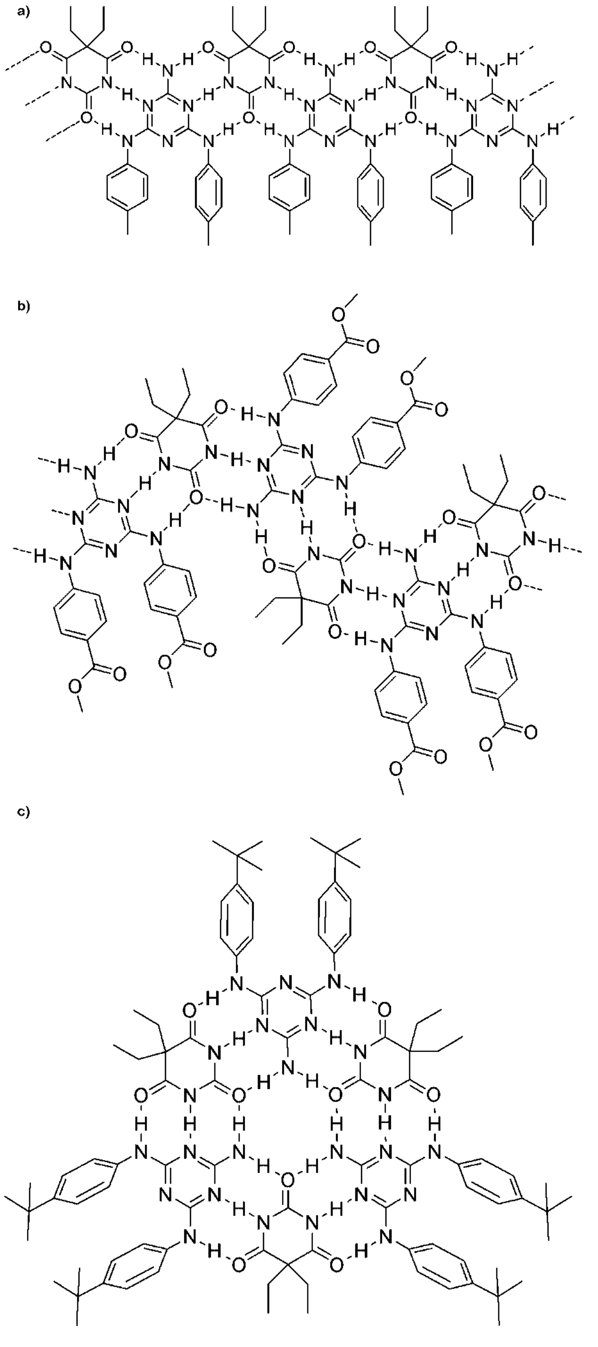


Figure 5. Structures of linear tape, crinkled tape, and rosette motifs.[16]

It has thus been evidenced that a competition takes place between nonbonded steric interactions (*para*-substituents) and a tendency for a high packing coefficient which is important in determining which type of structural motif is realized between the melamine derivative and 5,5-diethylbarbituric acid.[16] As a result, a small *para*-substituent like a methyl or a chloride group leads to a linear tape. If this substituent becomes larger than a trifluoromethyl unit, steric interactions between adjacent melamines prevent the linear structure and favour the crinkled motif where the hin drance is minimized. When the size of the *para*-substituent is further increased, to a *tert*-butyl group for example, then the steric interactions are relieved in the rosette type assembly.[16]

More recently, Reinhoudt and coworkers have beautifully developed the above concept to design and prepare more intricate H-bonded networks.[33,34] Thus, molecular cage hosts can be generated by self-assembly of calixarene-based melamine derivatives and diethylbarbituric acid.[35] A non-covalent phenolic receptor has been successfully prepared by hydrogen-bonding directed association of a calixa[4]rene dimelamine compound with diethylbarbituric acid (Figure 6).[36]

For instance, the simple mixing of the building blocks **1** (1 equivalent) and DEB (2 equivalents) in an apolar solvent like chloroform or toluene produces the double rosette $\mathbf{2}_3\cdot(\mathrm{DEB})_6$ (Figure 7). The formation of this calixarene-bridged supramolecular structure can be followed by solution ^{1}H NMR spectroscopy.

$\mathbf{2}_3\cdot(\mathrm{DEB})_6$ holds six H-donor/acceptor side-arms which can act as phenol binding sites by means of H-bonds between a urea function [Figure 6, $R^1 = R^2 = \mathrm{CONH(CH_2)_2CH_3}$] and the phenolic guest (Figure 7, G). The complexation of 4-nitrophenol by $\mathbf{2}_3\cdot(\mathrm{DEB})_6$ has been investigated by proton NMR spectroscopy at room temperature in $CDCl_3$. This comprehensive study clearly demonstrates that the double rosette is an *exo*-receptor able to accommodate six molecules of phenolic guest (one phenol unit per ureido group).

Last year, Meijer and coworkers reported another remarkable supramolecular rosette motif which has been evidenced by scanning tunnelling microscopy (STM).[37] For

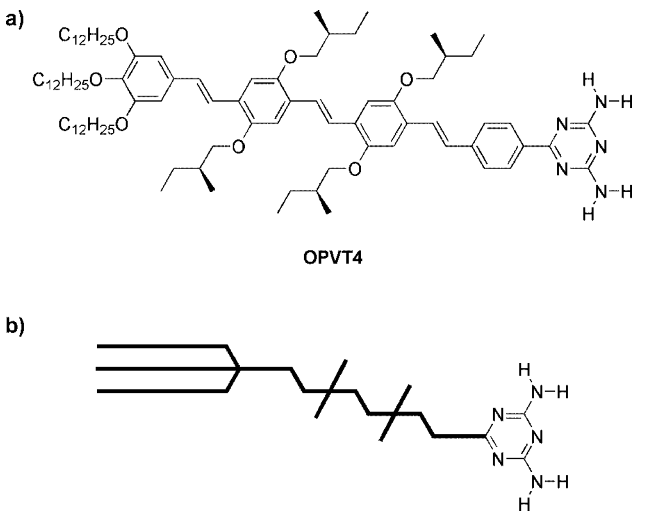


Figure 8. a) Melamine-based π-conjugated ligand OPVT4 and b) its schematic representation.[37]

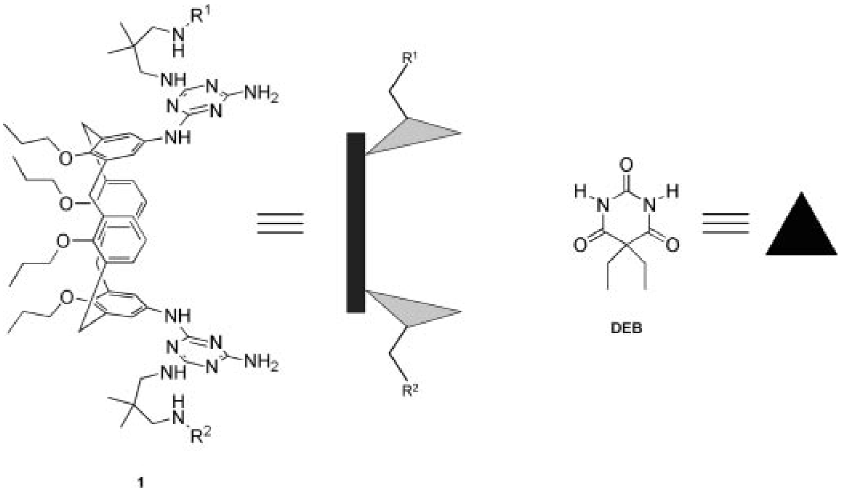


Figure 6. Building blocks for the formation of a double rosette assembly.[36]

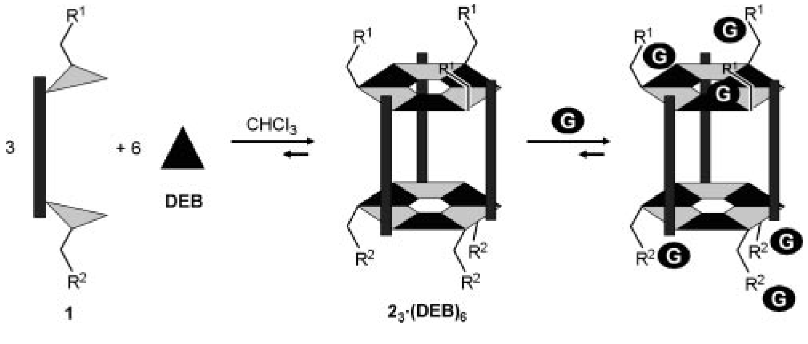


Figure 7. Schematic representation of the formation of the host–guest supramolecular double rosette system.[36]

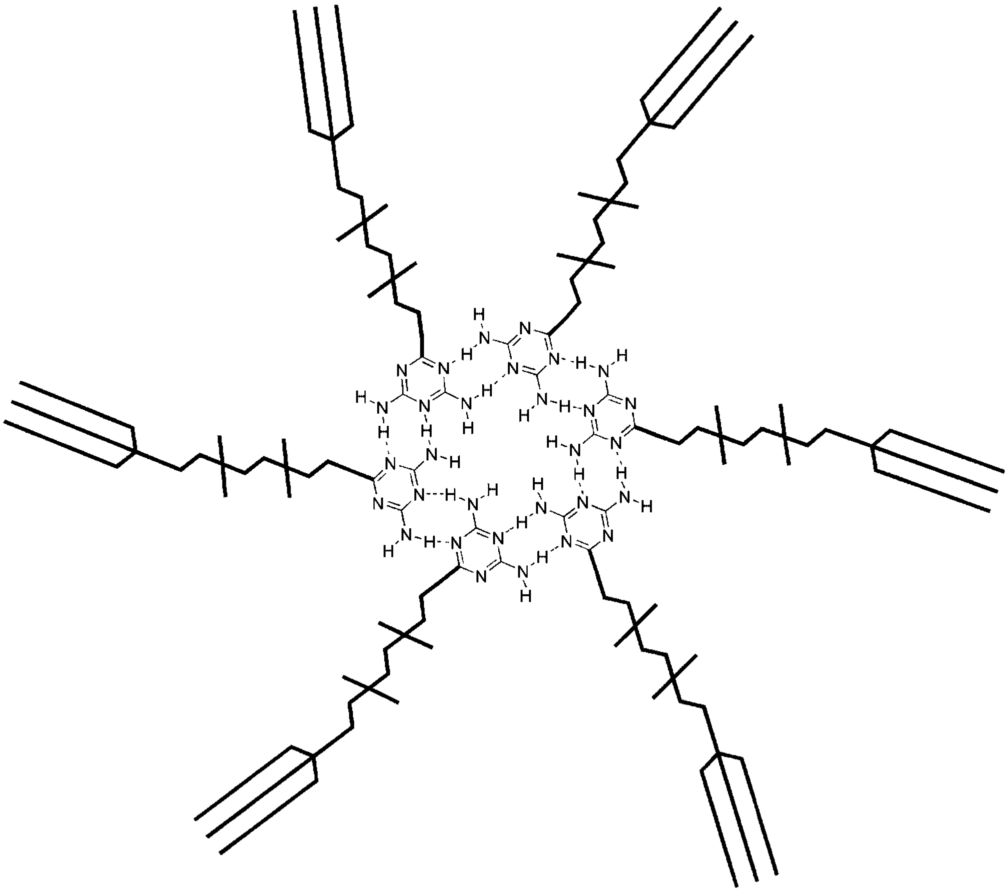


Figure 9. OPVT4 rosette.[37]

this purpose, the triazine-based ligand OPVT4 has been synthesized according to a reported procedure (Figure 8).[38] In solution in heptane, six OPVT4 molecules give a giant helical rosette with a width of about 10 nm (Figure 9).[37] This exceptional aggregation process has been followed by UV/Vis and circular dichroism (CD) in heptane and temperature-dependent measurements show that the rosette is dissociated at elevated temperature ($T = 305$ K).

In addition, the hydrogen-bonded hexamer is chiral as proven by CD and by the counterclockwise rosette structure clearly visible in the STM images.[37] These rosettes can be stacked together to form fibres with lengths up to 10 µm as revealed by atomic force microscopy (AFM). The self-assembled tubular aggregates 6.4 nm in diameter are still soluble in heptane owing to the peripheral apolar alkyl chains (Figure 10).

The cavity generated by the formation of the hexameric rosette is about 1 nm wide and contains amine groups which would therefore find application as an ideal channel for transportation. Furthermore, the tubular stacks exhibit a well-defined and ordered π-conjugated outside shell with probable electronic properties.

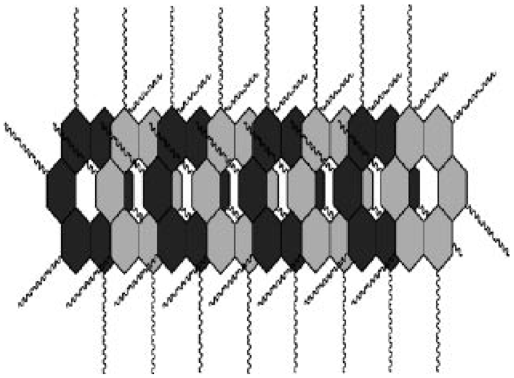


Figure 10. Rosette stacks leading to a tubular fibre.[37]

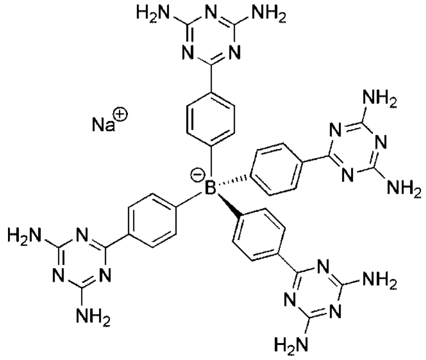


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Figure 11. Sodium tetrakis[4-(2,4-diamino-[1,3,5]triazin-6-yl)-phenyl]borate (**2**·Na).[39]

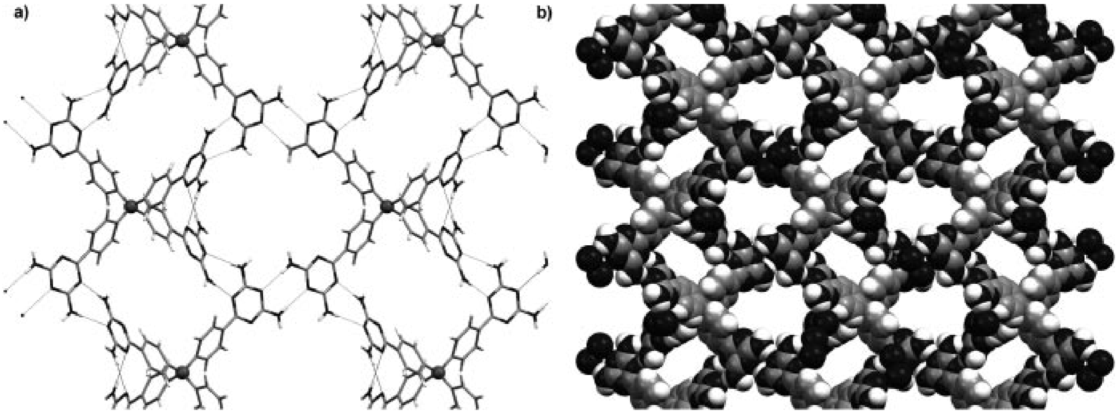

Figure 12. a) Anionic H-bonded network **2**. b) Interconnected channels.[39]

Very recently, Wuest and coworkers designed and synthesized a 3D triazine-based synthon, i.e. the tetraphenylborate Na·**2** (Figure 11).[39] The tetraphenylphosphanium salt of **2** is obtained quantitatively from the sodium salt by cation exchange. Single crystals of tecton PPh_4·**2** have been grown from a DMSO/toluene solution of the compound, whose solid-state structure reveals an aesthetic three-dimensional network, connected by multiple hydrogen bonds as expected (Figure 12). This anionic supramolecular architecture is extremely porous (Figure 12b), since 74% of the volume of the crystals is available for cations and guest molecules (DMSO in the present study). Materials with such great porosity are very important in the field of gas storage,[40] especially for fuel-cell applications.[41,42]

In addition, the cation can be exchanged within the crystalline solid compound. Thus, the same anionic framework is achieved when using phenazinium cation **3** (Figure 13) instead of tetraphenylphosphonium. These crystals of tecton **2** with phenazinium **3** as the counterion have been exposed to a solution of an excess of PPh_4Br in DMSO for 24 h at room temperature. The resulting material remains transparent and crystalline, and diffracts with unit cell parameters analogous to those of PPh_4·**2**. This is an important result as a larger cation, **3**, has been replaced by a smaller one, namely tetraphenylphosphanium. Indeed, such exchange releases space within the porous material, which is available for additional neutral guest molecules. This finding gives rise to a novel approach of crystal engineering where new ionic host–guest materials can be produced by substitution of the initial cations to increase their porosity and/or physical properties without modification of their molecular arrangement.

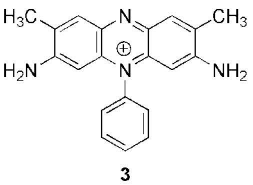

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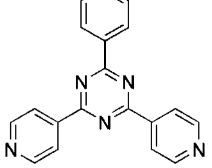
Figure 13. Phenazinium cation **3**.

4. 1,3,5-Triazine Derivatives as Ligands for the Preparation of Coordination Self-Assemblies

Coordination compounds from 1,3,5-triazine-based ligands are increasingly reported in the literature.[43–48] This is undoubtedly due to the ease of preparing intricate polydentate star-shaped ligands using simple and high-yielding reactions.[23] Especially one ligand, namely 2,4,6-tri(4-pyridyl)-1,3,5-triazine (Figure 14, tpt), has been extensively used in the field of crystal engineering during the past ten years.[47,49] However, novel and attractive supramolecular architectures continue to be obtained with this simple tridirectional N-donor ligand.[50] Robson's group[49] published the first crystallographically characterized coordination polymer based on tpt 24 years after it was primarily reported by Yasumoto and coworkers.[51]



tpt

Figure 14. 2,4,6-tri(4-pyridyl)-1,3,5-triazine ligand (tpt).[49,51]

In 1996, Robson and coworkers described a unique system of two interpenetrating coordination networks based on tpt and copper(I) building blocks (Figure 15a).[52] The infinite (3,4)-connected network is built from repeated structural motifs with six copper centres at the corners of a regular octahedron (Figure 15b), each copper ion being shared by two adjacent motifs. This arrangement results in an infinite cubic collection of 18-Å-wide octahedral cavities filled with solvent molecules.

Almost at the same time, Fujita and coworkers reported a similar octahedral cage assembled from tpt and palladium(II) nodes.[53] The reaction of six equivalents of the Pd^{II} complex **4** with four equivalents of tpt leads, in water, to the exclusive and quantitative formation of the supramolec-

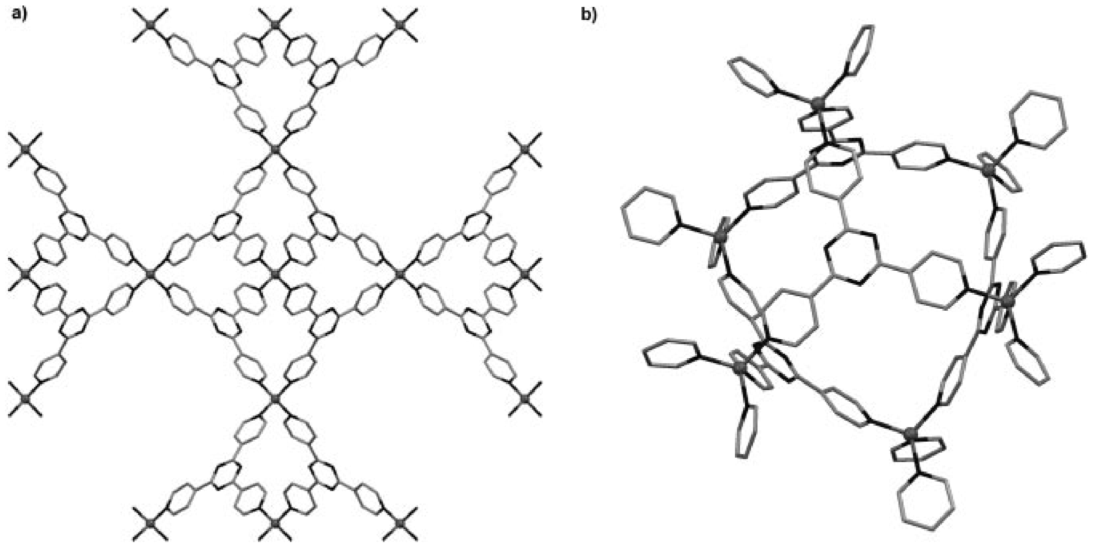


Figure 15. a) Cubic (3,4)-connected net. b) Octahedral host chamber.[52]

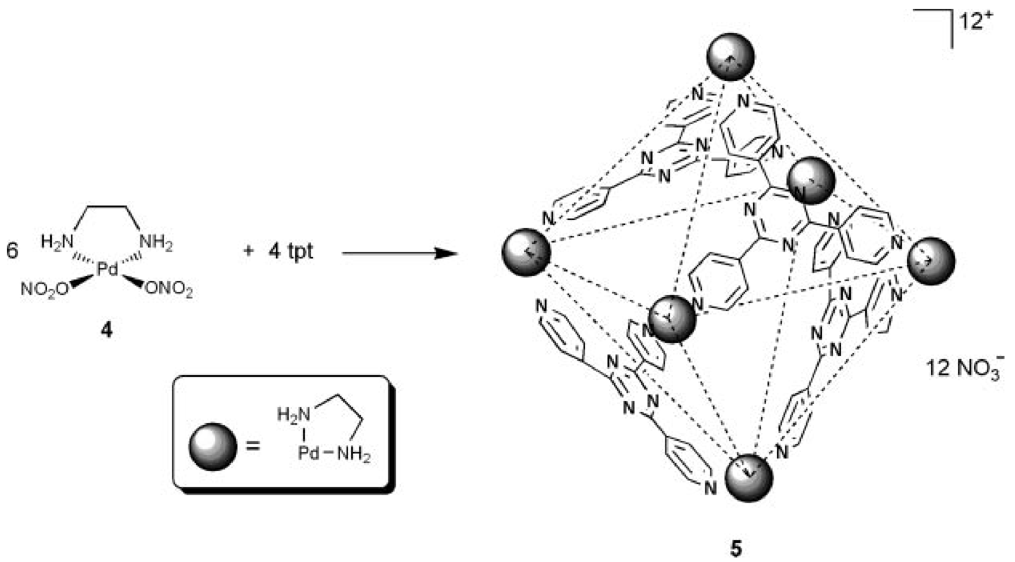


Figure 16. Self-assembly of a nanometer-scale octahedral cage.[53]

ular cage **5** (Figure 16).[53] The assembly of complex **5** has been followed by ^{1}H NMR spectroscopy, which clearly demonstrated that the M_6L_4 compound is the thermodynamic product since its formation is not affected by the presence of an excess of **4**.

It has been shown that this coordination cage can bind efficiently various organic guest molecules[54,55] including radicals[56] as well as a water cluster[17] in its cavity. For example, *o*-carborane, an icosahedral carbon–boron cage molecule with a diameter of 8 Å, can be encapsulated in **5**.[57] This spherical, neutral molecule is apolar and insoluble in water. However, when a hexane solution of *o*-carborane is stirred with a D_2O solution of **5**, four equivalents of *o*-carborane are transferred into the D_2O phase to form **5**·(*o*-carborane)$_4$, as evidenced by ^{1}H NMR spectroscopy. This host–guest complex has never been crystallized, but the analogous compound having 2,2′-bipyridine as *cis*-protecting ligand in place of ethylene diamine is easily crystallized in water (Figure 17).[54]

Fujita and coworkers then tried to use these cavities to perform catalytic reactions.[58] The palladium-catalyzed Wacker oxidation of styrene has been carried out in water with **5**, which can accommodate three molecules of styrene (**6**) in its cavity.[58] If the reaction is achieved at 80 °C with **4** or with **5**, only 4% of acetophenone (**7**) is detected. If the oxidation is performed in the presence of both **4** and **5**, then the yield in acetophenone is significantly increased to 86% (Figure 18a). Similarly, the ability of **5** to promote the isomerization of allylbenzene (**8**) has been examined. Once again, while the reaction does not occur in the absence of either **4** or **5**, 50% of β-methylstyrene (**9**) is obtained when a 2:1 mixture of **4** and **5** is used (Figure 18b).[59] Complex **5** acts as a phase-transfer reagent which brings the substrate, i.e. the organic molecule **6** or **8**, into the aqueous

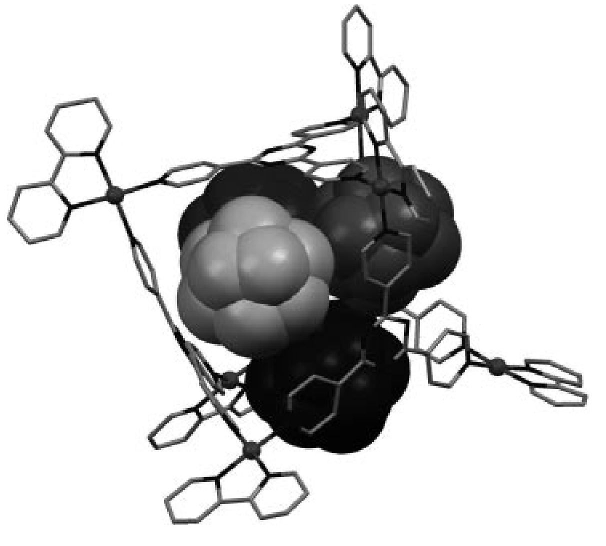


Figure 17. Encapsulation of four *o*-carborane in an M_6L_4 cage.[57]

phase where the palladium-mediated chemical transformation takes place. These outstanding results represent good examples of solvent-free organic reactions.

More recently, we have undertaken research investigations on coordination networks involving *s*-triazine-based N-donor ligands. For this purpose, a series of polydentate ligands have been prepared[23,60,61] according to the synthetic pathway depicted in Figure 2, and some of them are reported in Figure 19.

The simple dpyatriz ligand arises from the substitution of the three chlorides of cyanuric chloride by 2,2′-dipyridylamine and has been reported by some of us[23] and by Wang and coworkers.[62,63] Reaction of Cu^{II} nitrate with dpyatriz in acetonitrile at room temperature produces a 1D ladder coordination polymer, whose crystal structure is depicted in Figure 20.[61] The polymeric compound is built up from pentanuclear copper units which are bridged by bidentate nitrate anions (Figure 20b). This uncommon molecular network[3] possesses large rectangular guest cavities with dimensions of approximately 10 × 5.5 Å, which are filled with seven acetonitrile molecules.[61] Thus, the uncoordinated solvent molecules cover 25% (652 Å^3) of the unit cell volume.

Thermogravimetric analysis (TGA) of the polymeric material shows 11.1% loss in weight, which exactly matches seven acetonitrile molecules. A second TGA experiment on the acetonitrile-free crystalline material left in air shows a decrease of 18.8% in weight. This decrease is attributed to the loss of water molecules rapidly taken up by the initial

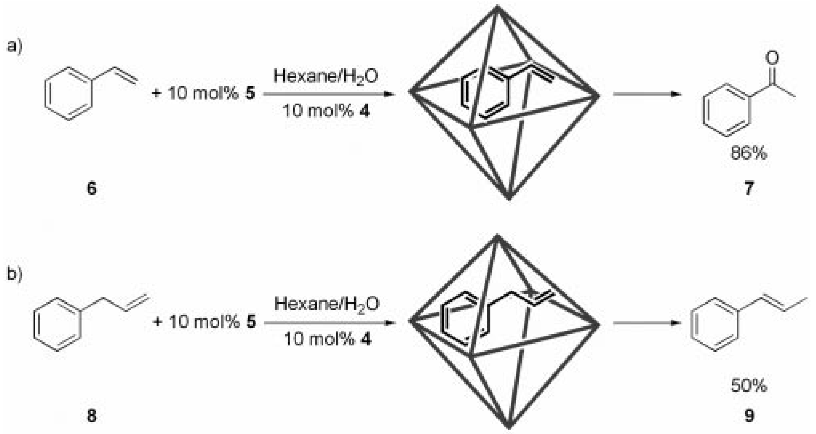


Figure 18. a) Wacker oxidation in the M_6L_4 cage.[59] b) isomerisation of an alkene in the M_6L_4 cage.[58]

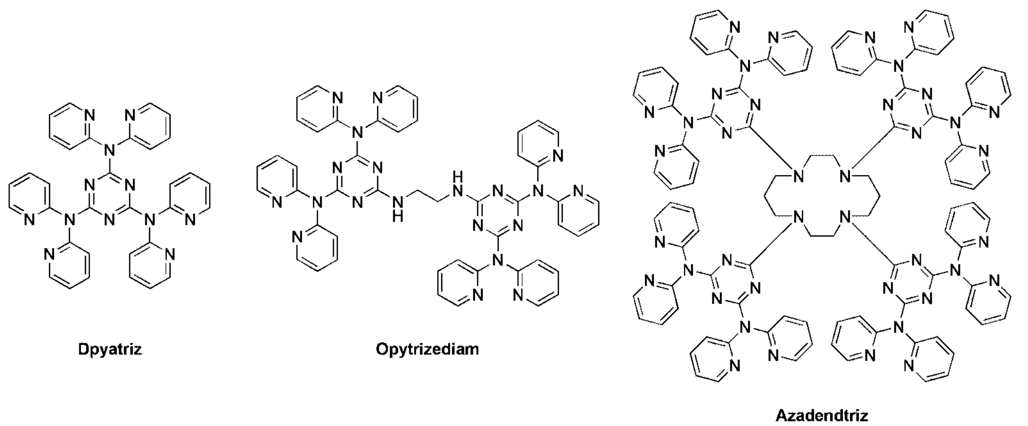


Figure 19. *s*-Triazine-based ligands used to prepare supramolecular coordination compounds.[61,64,66]

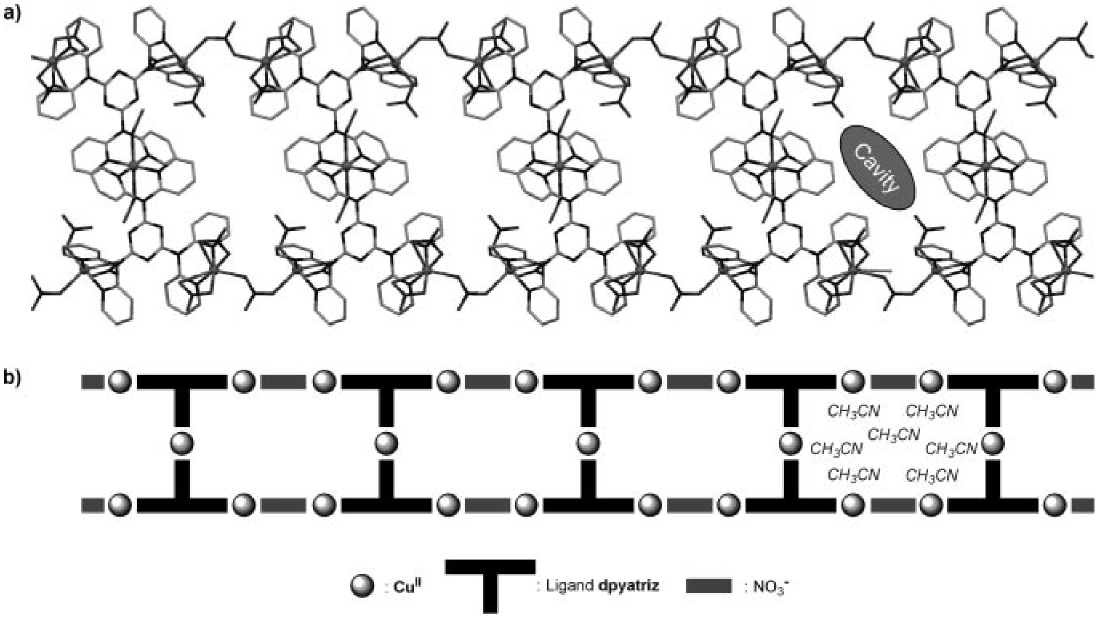


Figure 20. a) 1D ladder coordination polymer obtained from the ligand dpyatriz and $Cu(NO_3)_2$; and b) its schematic representation.[61]

material after removal of the acetonitrile molecules. This result demonstrates the possibility of using this 1D ladder coordination polymer in host–guest molecular recognition.

Another attractive coordination compound has been obtained by our group from the extended ligand opytrizediam (Figure 19). Indeed, the reaction of copper(II) chloride with this ligand in methanol leads to the formation of a 1D zigzag coordination polymer (Figure 21).[64] The polymeric compound is composed of trinuclear copper units that are connected by means of chloride bridges in a zigzag fashion, since the ligands are *up* and *down* alternated (Figure 21b). Despite its unusual arrangement,[3] this material exhibits interesting physical properties. First, a large amount of solvent molecules is present in the crystal lattice (29% of the unit cell volume, 1016 Å^3). The removal of these molecules may create space for the sorption of gases such as dinitrogen and dihydrogen. This is a vital feature in the field of fuel cell chemistry.[41,42,65] Second, the coordination polymer possesses ferromagnetic properties [$J = 6.4(1)\ \mathrm{cm}^{-1}$] inherent to the doubly chloro-bridged dicopper moieties linking the complexes to generate the infinite chain.

Recently, a very important finding in the field of anion recognition has been achieved by using the dendritic ligand azadendtriz (Figure 19).[66] Indeed, anions are ubiquitous in biochemical structures.[67,68] Contrary to that of cations, the binding of anions has received little attention. However, during the past two decades, an increasing number of anion receptors have been developed,[69,70] most likely because of their potential applications in medicine, biology, catalysis, or for the elimination of anionic polluting wastes.[71]

A number of recent publications have reported theoretical investigations on the binding of halides with the electron-deficient *s*-triazine ring.[72] All calculations clearly indicate energetically favourable noncovalent interactions between the halide and the electron-poor aromatic ring.[73,74] Consequently, *s*-triazine-based compounds are perfect candidates for the development of anion host chemistry. This

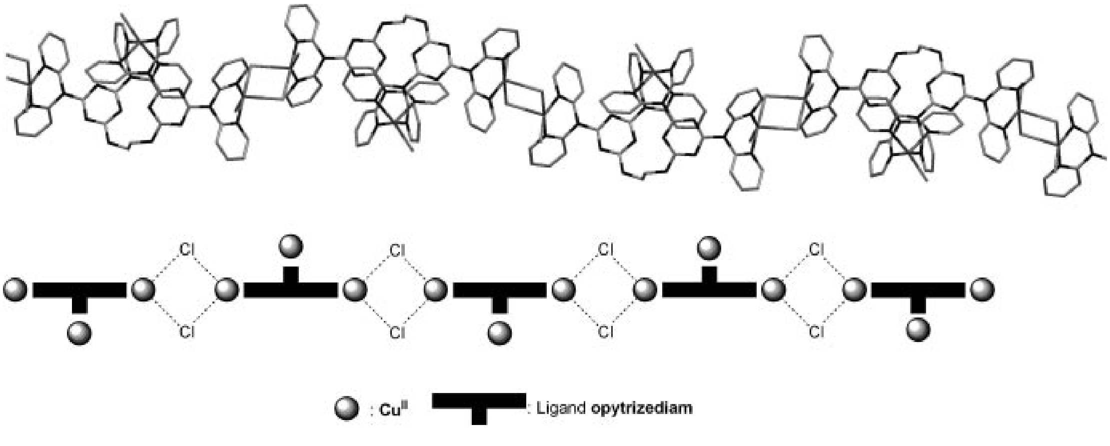


Figure 21. a) 1D zigzag coordination polymer obtained from the ligand opytrizediam and $CuCl_2$; and b) its schematic representation.[64]

property was recently evidenced by the first crystallographic proof of such interactions.[75]

Reaction of copper(II) chloride with the ligand azadendtriz (Figure 19) in dichloromethane/water yields the tetracopper complex depicted in Figure 22a, where the triazinyl groups are stacked two by two in a parallel mode. This is often observed in triazine rings and is known as the Piedfort effect.[76] As a result, the copper ions are coordinated by two 2,2′-dipyridylamino units from two different *s*-triazine rings, generating two aromatic baskets, each formed by four pyridines (Figure 22b). These open cavities act as anion receptors for two chlorides through anion-π interactions. In addition, the chloride ions are close to the neighbouring triazine rings (Figure 22a), suggesting electrostatic interactions between the guest and the electron-deficient triazine moieties. Thus, the combination of both electronic effects produces the first non-hydrogen-bonding artificial anionic receptor.

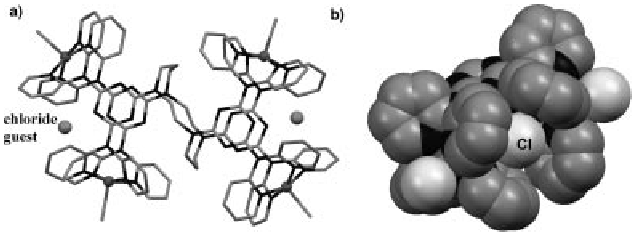


Figure 22. a) [$CuCl_2$–azadentriz] complex showing anion-binding properties; b) guest chloride anion embraced between four pyridine rings.[66]

Finally, the influence of the temperature and the pressure on the nature of the coordination framework obtained has been clearly demonstrated by using the ligand dpyatriz (Figure 19).[77] The reaction of zinc(II) nitrate with dpyatriz in acetonitrile at room temperature gives a tetranuclear zinc complex accommodating two triazine-based ligands (Figure 23).[78]

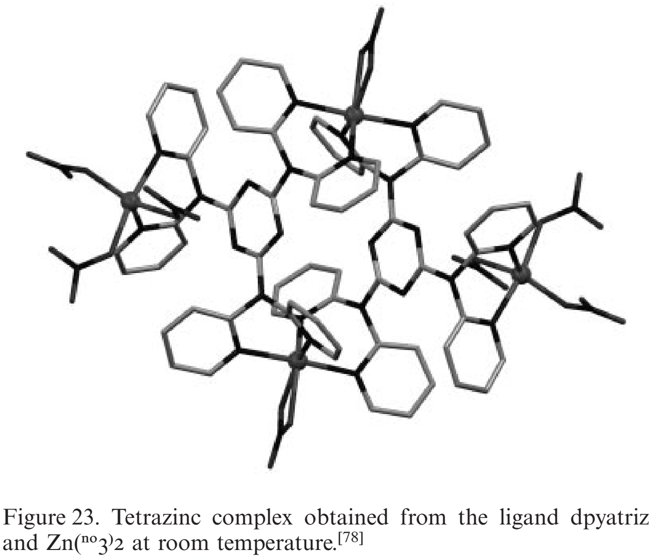


Figure 23. Tetrazinc complex obtained from the ligand dpyatriz and Zn(^{no}3${}^{)}$2 at room temperature.[78]

However, if the same reaction is performed in a sealed tube at 105 °C under autogenous pressure, a 1D polymeric chain is obtained (Figure 24).[77] The significantly different crystal packing observed at different crystallisation conditions illustrate the difficulty of anticipating a crystal structure. Crystal engineering involves various interactions between the synthons (ligand, metal ion, anion, solvent). In addition, the temperature and the pressure applied during the experiment are obviously important and hence should be considered for a better prediction of the crystal structure.

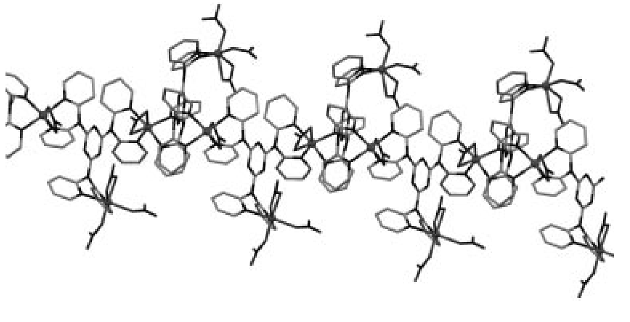


Figure 24. Coordination polymer obtained from the ligand dpyatriz and $Zn(NO_3)_2$ at 105 °C under autogenous pressure.[77]

A closely related 1D coordination polymer is achieved with copper(II) nitrate [in place of $Zn(NO_3)_2$] using the same crystallisation process, while a 1D ladder network is obtained at room temperature and normal pressure (Figure 20 and Figure 24).[61,77]

5. 1,3,5-Triazine Derivatives Combining Both H-Bonding and Coordination Interactions

There are only a few examples reported in the literature where the H-bonding ability of melamine derivatives has been used in combination with coordination bonds. Lehn and coworkers have described, in 1995, an ion-labelling system to detect by mass spectroscopy the formation of H-bonded networks by the binding of a metal ion, namely potassium(I).[79] The triazine **10** (Figure 25a) has been syn-

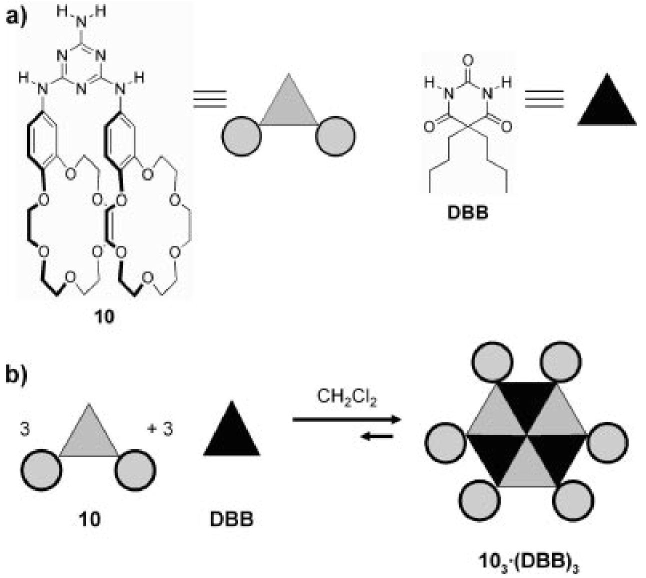


Figure 25. a) Benzocrown-containing triazine-based ligand **10**. b) Formation of the rosette assembly.[79]

thesized in 76% yield by reaction of two equivalents of 4′-aminobenzo[18]crown-6 with one equivalent of 6-amino-2,4-dichloro-1,3,5-triazine. The H-bonded self-assembly of **10** with 5,5-dibutylbarbituric acid (DBB) can lead to the formation of various architectures, namely linear tape, crinkled tape or rosette (Figure 5 and Figure 25b).

Equimolar 10^{-2} M solutions of **10** and DBB in dichloromethane are combined and treated with KPF_6. The resulting mixture is then analysed by electrospray mass spectrometry (ESMS), which shows ion compositions characteristic for the free ligand **10** and for the self-assemblies $\mathbf{10}_2$·(DBB)$_3$, $\mathbf{10}_3$·(DBB)$_2$ and $\mathbf{10}_3$·(DBB)$_3$. The addition of methanol (which is known to disrupt H-networks) to this reaction mixture causes the disappearance of all peaks due to $\mathbf{10}_x$·(DBB)$_y$ complexes, supporting their presence in the initial solution, since no additional assembly is observed in the gas phase (after addition of methanol). These ESMS studies clearly demonstrate the possibility of using this technique with weakly associated self-assemblies which are destroyed by protonation. The ingenious stratagem consists then of introducing a charge through cation binding to a well-designed synthon such as **10**. In that way, a component like **10** in the presence of a salt forms a neutral supramolecular coordination species that cannot be otherwise characterised by ESMS.[79]

In 1998, Reinhoudt and coworkers developed a similar labelling method for the characterisation of double rosette assemblies, comparable to $\mathbf{2}_3$·(DEB)$_6$ (Figure 7), by MALDI-TOF mass spectrometry.[80] For this purpose, the ligand **11** has been prepared (Figure 26).

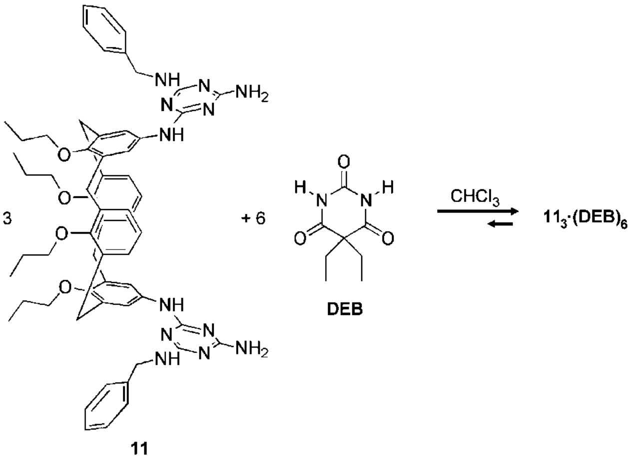


Figure 26. Components used to prepare the double rosette assembly.[80,81]

The $\mathbf{11}_3$·(DEB)$_6$ adduct obtained by mixing **11** and DEB is then stirred with 1.5 equivalents of Ag(CF_3COO) in chloroform for 24 h. Afterwards, the solution is analysed by MALDI-TOF mass spectrometry which shows an intense signal at *m/z* = 4278.3 (calculated value: 4276.1), ascribed to the silver(I) complex of $\mathbf{11}_3$·(DEB)$_6$ (Figure 27).[80] Moreover, these MS data are in perfect accordance with the ^1H NMR spectra of the hydrogen-bonded supramolecules in solution.

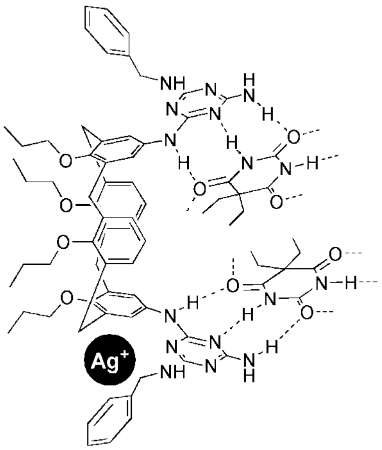
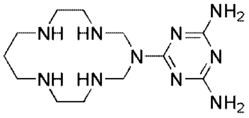


Figure 27. Proposed structure for the silver(I) complex of $\mathbf{11}_3$·(DEB)$_6$. Only a small part of the double rosette is shown for clarity.[80]

This silver(I) labelling technique has been extended to a variety of hydrogen-bonded assemblies and can be considered as a powerful tool to characterise noncovalent assemblies or host–guest complexes.[81]

In 1998, Bernhardt and coworkers[82] have reported the synthesis of a remarkable ditopic triazine-based ligand, namely [6-(4′,6′-diamino-1′,3′,5′-triazinyl)-1,4,6,8,11-pentaazacyclotetradecane] (**12**, Figure 28).



12

Figure 28. [6-(4′,6′-Diamino-1′,3′,5′-triazinyl)-1,4,6,8,11-pentaazacyclotetradecane] (**12**).[82,83]

As expected, this ligand can both bind a metal ion and be involved in the formation of a hydrogen network.[82,83] More recently, Bernhardt and coworkers have used this ligand to obtain a redox-active receptor for neutral guests.[84] The H-bonding abilities of the complex [Cu(**12**)]$^{2+}$ are obviously due to the presence of a melamine unit that can act as a donor–acceptor–donor entity (Figure 4). This intrinsic property has been used by Bernhardt and coworkers who have prepared a [Cu(**12**)]$^{2+}$/barbiturate adduct whose crystal structure is depicted in Figure 29.

H-bonded assemblies with barbitone and thymine (Figure 30) have also been obtained and crystallographically characterised. Solution electrochemical studies have been carried out in order to check the possibility of using [Cu(**12**)]$^{2+}$ as a redox-active receptor. The electrochemical detection is based on a shift of the redox potential of the host [Cu(**12**)]$^{2+}$ complex upon binding of the neutral guest molecule, i.e. barbitone, thymine, biuret or cytosine (Figure 30). These investigations have shown that the addition of complementary guests such as barbitone or biuret, which have an acceptor–donor–acceptor H-bonding pattern, leads to a significant shift in the Cu^{II}/Cu^{I} redox potential. On the

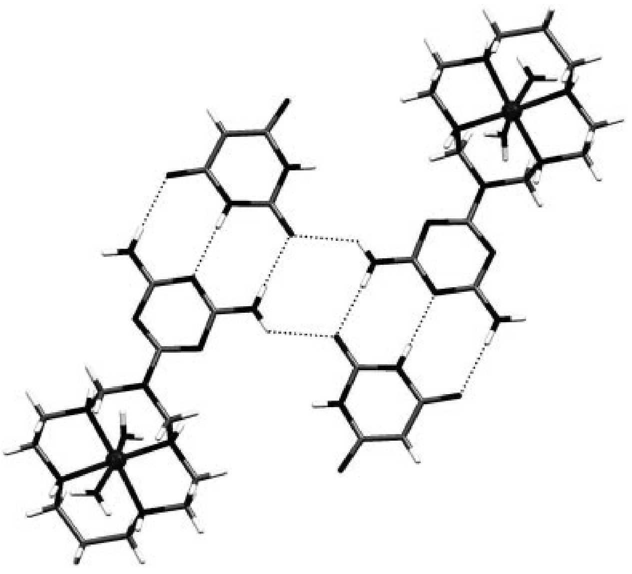


Figure 29. [Cu(**12**)]$^{+2}$/barbiturate H-bonded network.[84]

contrary, no significant shift has been observed with cytosine, which has a donor–acceptor–acceptor H-bonding pattern, mismatched with the donor–acceptor–donor pattern of [Cu(**12**)]$^{2+}$. The communication between the H-bonded element and the coordination unit of the triazine-based molecule has thus been clearly established and a host–guest selectivity has been evidenced. This type of material may be used as a sensor to detect specific polar organic compounds in solution.

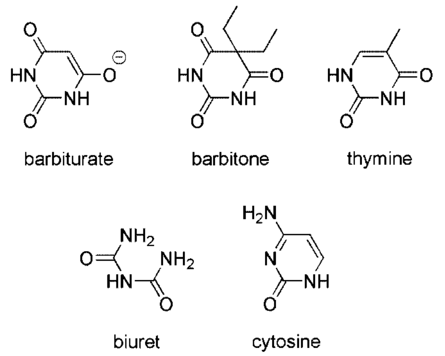


Figure 30. Guest molecules used with the complex [Cu(**12**)]$^{+2}$.[84]

6. Concluding Remarks

The vast development of supramolecular chemistry over the past twenty years has led to a huge diversity of chemical assemblies, obtained both by design[5] and serendipitous formation.[85] Tremendous progress has been made in the field of crystal structure prediction, using well-designed ligands and the reticular synthesis approach.[5] 1,3,5-Triazine-based synthons have proven their huge potential in this area, and the present microreview reports on some of the most remarkable examples published so far. The ability of melamine derivatives to generate H-bond networks has been elegantly applied by several research groups to produce host–guest or porous materials. The straightforward synthetic routes to generate sophisticated star-shaped polydentate N-ligands have allowed the preparation of molecular cages with applications in catalysis or separation, coordination polymers with magnetic properties or host–guest cavities, and anion hosting materials. Finally, the judicious combinations of H-bonding and coordinative interactions through the use of well-designed 1,3,5-triazine building blocks have generated functional materials with applications in mass spectrometry labelling and in sensoring. As summarized above, triazine-based supramolecules are highly promising synthons for the design and synthesis of exciting new polyfunctional compounds. The controlled preparation of hybrid inorganic–organic materials has remarkably improved since the late 1990s, and the important challenge of the contemporary supramolecular chemist is now to control the functionalization of such solids.[5] This includes the capacity to design intricate ligands which will act both as structural and functional buildings blocks to prepare custom-made materials possessing one or more specific properties, which can certainly be envisaged starting from the inexpensive, readily available 2,4,6-trichloro-1,3,5-triazine.

Acknowledgments

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