

# The Design and Synthesis of Versatile Molecular Building Blocks: Working Towards the Controlled Self-Assembly of Novel Functional Materials

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**Abstract:** Our research goals are focused on the preparation of novel molecule-based materials that possess specifically designed properties in solution or in the solid state e.g. self-assembly, magnetism, conductivity and spin crossover phenomena. Most of our systems incorporate paramagnetic transition metal ions and the search for new molecule-based magnetic materials is a prominent theme. Specific areas of research include the preparation and study of oxalate based 2D and 3D magnets, probing the versatility of octacyanometalate building blocks as precursors for new molecular magnets, and the preparation of new tetrathiafulvalene (TTF) derivatives for applications in molecular and supramolecular chemistry.

**Keywords:** Magnetism · Molecule-based materials · Octacyanometalates · Supramolecular chemistry · Tetrathiafulvalene · Tris-oxalato complexes

## 1. Introduction

Driven by the onward decrease of component size in conventional electronics, chemists in recent years have begun to create some of the basic building blocks needed for the self-assembly of nano-scale molecular devices including metals, semiconductors, and molecule-based magnets. Consequently, it is to the realm of supramolecular chemistry that synthetic chemists are turning, in order to develop techniques for the synthesis of structurally well-defined materials with a predictable order and a useful set of solid-state properties [1]. Following this ap-

proach, we are currently investigating the versatility of three classes of molecular building blocks as precursors for the self-assembly of novel molecule-based materials.

## 2. Oxalate-based 2D and 3D Magnets

The field of oxalate-based 2D and 3D molecule-based magnets highlights the progress chemists have made in a relatively new area of materials chemistry, namely molecule-based magnets to address the concept of controlling intermolecular interactions in order to design crystal lattices with predictable structures [2]. In recent years, we have demonstrated that it is possible to develop a strategy for the controlled self-assembly of supramolecular systems based on transition-metal oxalates, which typically behave as host/guest compounds with different lattice dimensionalities (Fig. 1) [3]. All of these classes of structure are formally composed of metal-oxalate building blocks (Fig. 2). These compounds display a range of interesting magnetic properties, since the oxalate bridge is a good mediator of both antiferromagnetic and ferromagnetic interactions between paramagnetic metal centres.

## 3. Octacyanometalates – New Molecular Magnet Precursors

An alternative class of functional supramolecular materials is the three-dimensional network architectures self-assembled from cyanide ligands and metallic centres that carry a magnetic moment. Since the  $\mu$ -cyanide linkage permits an interaction between paramagnetic metal ions, cyanometalate building blocks have currently found useful applications in the field of molecule-based magnetism. We are currently exploring the versatility of the octacyanometalate building block  $[M(CN)_8]^{n-}$ , where M = transition metal ion, for the self-assembly of novel supramolecular coordination compounds. Along these lines, we have recently structurally and magnetically characterized a novel cyanide-bridged high-spin molecular cluster of stoichiometry  $[Mn^{II}\{Mn^{II}(MeOH)_3\}_8(\mu-CN)_{30}\{Mo^V(CN)_3\}_6] \cdot 5MeOH \cdot 2H_2O$ , prepared by the self-assembly of  $[Mo^V(CN)_8]^{3-}$  building blocks together with a  $Mn^{II}$  salt [4]. The cluster comprises 15 cyano-bridged metal ions, namely 9  $Mn^{II}$  ions ( $S = 5/2$ ) and 6  $Mo^V$  ions ( $S = 1/2$ ), giving a total of 51 unpaired electrons within the cluster. The  $Mo^V$ -CN- $Mn^{II}$  geometry is such that the atoms are all linked to form an aesthetically pleasing

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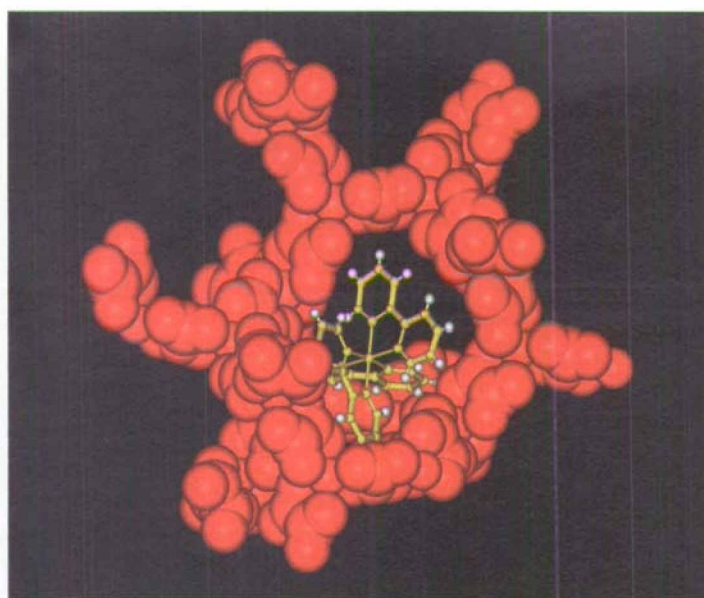


Fig. 1. A chiral 3D host/guest compound of stoichiometry  $[M^I(\text{bpy})_3][M^II(\text{C}_2\text{O}_4)_3]_n$ . Only one guest molecule is shown within the chiral framework.

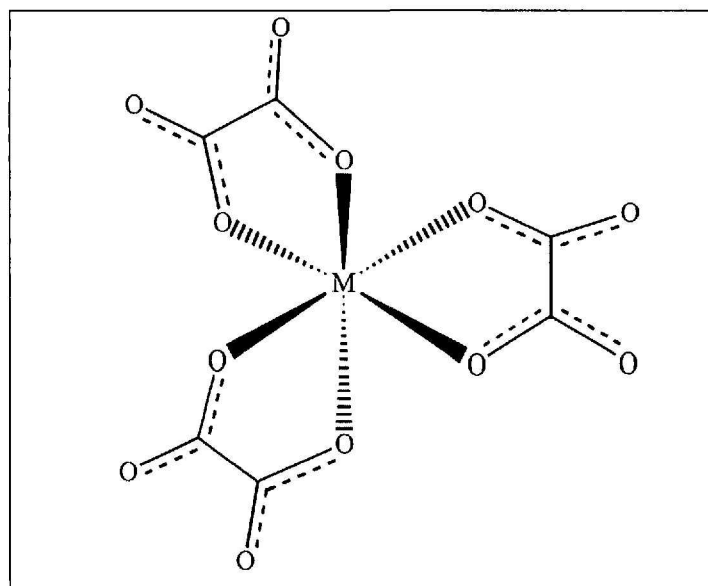


Fig. 2. Molecular building blocks, namely anionic, *tris*-chelated transition-metal oxalato complexes,  $[M^{z+}(\text{ox})_3]^{[6-2]-}$ ;  $\text{ox} = \text{C}_2\text{O}_4^{2-}$ . As a consequence of this type of connectivity, each coordinated metal ion represents a chiral centre with  $D_3$  point group symmetry, showing either  $\Lambda$ - or  $\Delta$ -helical chirality.

topological pattern in which the polyhedron spanned by the peripheral metal ions is closest in geometry to a rhombic dodecahedron (Fig. 3). The magnetic properties of the  $\text{Mn}^{II}_9\text{Mo}^V_6$  cluster above 44 K are characterized by ferromagnetic intra-cluster coupling, which finally leads to an  $S = 5\frac{1}{2}$  ground state spin.

#### 4. Tetrathiafulvalene Derivatives – Probing Their Potential for the Self-assembly of Novel Functional Materials

Molecular conductors have attracted much attention since the discovery of the

first organic metal, namely a charge transfer complex between TTF and TCNQ [5]. New developments in the synthesis of donor molecules have emerged over the last 20 years, and molecules based on large sulphur heterocycles have provided several new precursors for conducting materials [6][7]. Recent studies suggest that molecular conducting systems composed of transition metal complexes are providing a new approach in the area of molecular conductors [8]. For further advances in this field, the development of new systems is of prime importance, since very little is still known about the control of the  $\pi$ -d interactions in molecular metals. Our research in-

volves the covalent attachment of metal binding sites onto a TTF-type skeleton (Fig. 4) together with an investigation of the chemical and physical properties of new materials assembled from these molecular components. The design and study of organic conductors containing localised magnetic moments is also an area of interest, since the search for molecule-based materials combining properties not normally associated with a single material *e.g.* coupling conductivity or superconductivity with magnetism, constitutes one of the major challenges at the frontiers of materials chemistry today [9].

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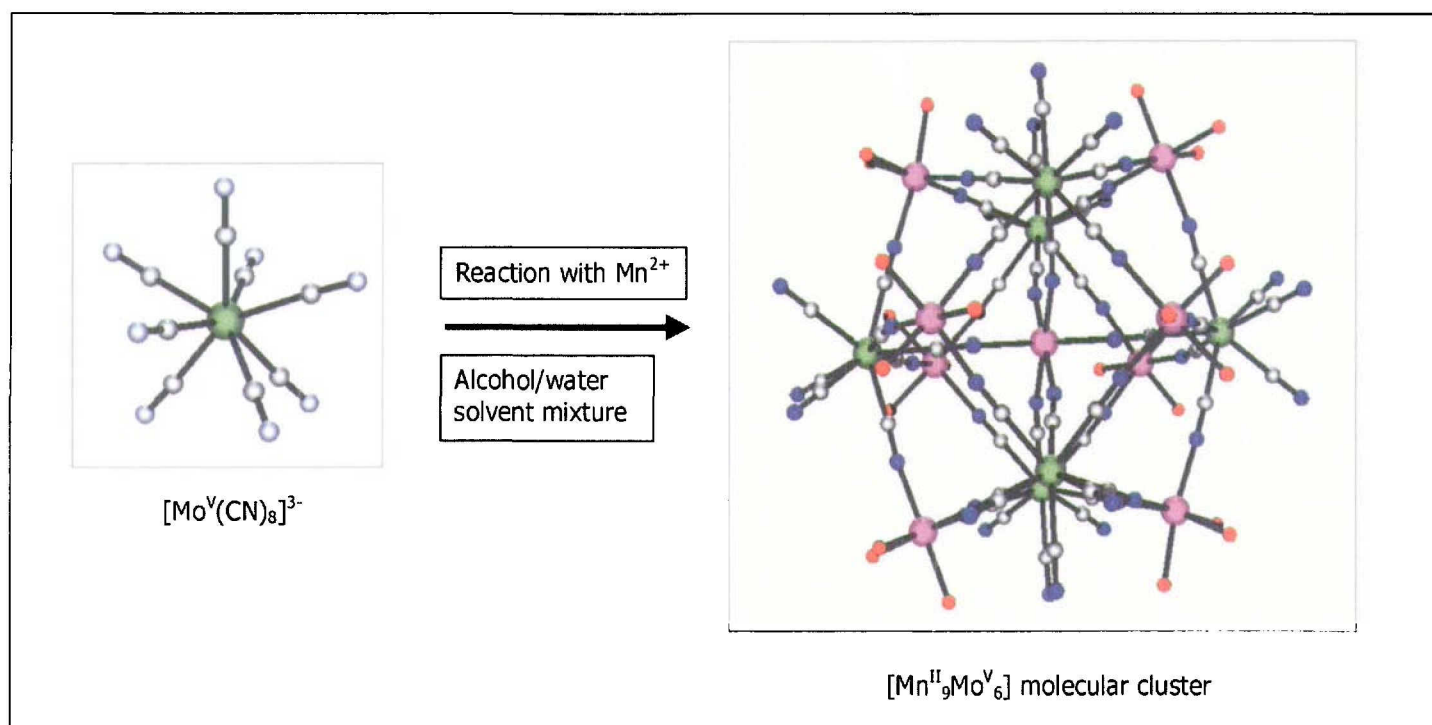


Fig. 3. The octacyanometalate building block (left) used for the self-assembly of a novel cyanide bridged  $[\text{Mn}_9^{\text{II}}\text{Mo}_6^{\text{V}}]$  high-spin molecular cluster (right).

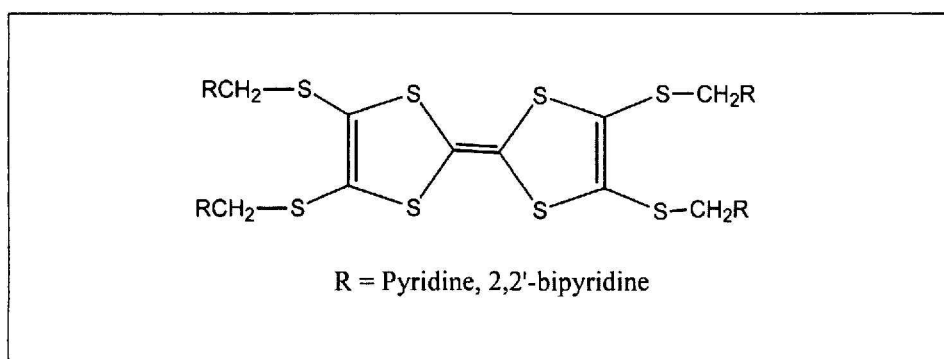


Fig. 4. TTF related building blocks with diimine binding sites covalently attached to the four peripheral sulphur atoms.

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