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Towards Molecular Wires Based on Metal-Organic Frameworks

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The formation of one-dimensional structures on nanoscale is one of the main goals of modern nanotechnology. The aim of these efforts is to find conductive long molecules that could serve as molecular wires in nanocircuits. In recent years, electrical conductivity in several organic and metal-organic systems has been studied to this end. In principle, DNA is one of the most attractive molecules for molecular wire owing to its well-known self-assembly chemistry and controllable structural diversity. However, the ability of DNA to conduct electricity is still controversial. In principle, binding of metal ions to organic molecules seems to be a suitable method for improving conductivity. Therefore, some studies were carried out with the so-called M-DNA as an alternative to increase conductivity on DNA. We have selected the 1D-coordination polymer $[Cd(6\text{-}MP^{-})_2]_n$ (6-MP⁻ = 6-mercaptopurinate) as a feasible structural model that is suitable for providing basic information about the electrical properties of M-DNA.Work with this coordination polymer revealed several aspects concerning the systematic search for new adsorption methods for coordination polymers on surfaces, their morphological and physical characterization, and opened a new playground for the study of coordination polymers as potential molecular wires. In this microreview, we focus on the description of several methods dealing with the isolation of single chains from crystals of these supramolecules, and different pathways to obtain molecular assemblies are also described. Methodologies and characterization techniques are illustrated with the results obtained with different coordination polymers.

1. Introduction

In modern technology, the performance of a variety of devices directly depends on the level of miniaturization reached. This is why nanotechnology has attracted so much interest in recent years. One of the ultimate goals of nanotechnology is to generate well-organized functional systems based on molecules in order to reach the highest possible level of miniaturization. A widely used strategy to generate miniaturized systems consists of a variety of nanolithographic methods. However, this requires complex and expensive instrumentation and the level of miniaturization reached is usually far from the molecular scale. However, bottom-up alternatives have been developed. The basis of bottom-up methods lies in the ability of specific single molecules to self-organize and generate supramolecules in a similar fashion to how nucleic acids work in nature. However, the predictable self-assembly of basic molecular subunits to obtain specific desired architectures is still an important challenge for chemistry.[1]

Envisaging applications on molecular electronics, the bottom-up design of molecular wires has been explored intensively over the last decade.[2] A molecular wire can be defined as a molecule that is able to transport electrical current between two points of a circuit.[3] They are essential building blocks for the fabrication of molecular circuits. However, in most studies of molecular wires, electrical conductivity experiments with single molecules have been never tested and this term has been coined from a merely structural point of view, or just taken into account electrical conductivity measurements in bulk. This problem has been closely related with the experimental limitations of these measurements.

DNA is an attractive molecule to be considered a candidate for molecular wire because it presents a well-known self-assembly chemistry in terms of the design of sequences, a facile coordination of metals, and an astonishingly controllable structural diversity.[4,5] However, the ability of DNA to conduct electricity is still a matter of debate.[6,7]

On the other hand, carbon nanotubes (CNTs) are other potential candidates since they show excellent electrical properties.[8] However, several problems related with low

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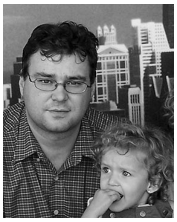
solubility and the difficult selective functionalization of CNTs preclude their suitability for the fabrication of molecular circuits.[9]

To date, the electrical properties of other systems based on molecules have been studied. Most of the works have centered on organic molecules and, very few on inorganic molecules, including metal-organic systems. A remarkable feature of these systems is the length of the molecules used to carry out the electrical single-molecule measurements. With the exception of DNA and CNTs, the typical lengths of organic and inorganic molecules usually fall in a narrow range (ca. 1–20 nm). This is an issue that needs to be ad-



Dr. Rubén Mas-Ballesté was born in Barcelona (Catalonia), Spain, in October 1975. He studied Chemistry at the Universitat Autónoma de Barcelona where he obtained his BSc. degree in Chemistry in June 1998, and his Ph.D. in February 2004 under the supervision of Prof. Pilar González-Duarte and Prof. Agustí Lledós. From June 2004 to November 2007 he worked in the Lawrence Que group at the University of Minnesota (USA) as a postdoctoral associate. He is now an associate professor under the "Ramón y Cajal" program at the Universidad Autónoma de Madrid (Spain). His research interests are the reactivity of metal chalcogenides, the synthesis and reactivity of structural and functional models of metalloproteins and inorganic compounds of interest in nanotechnology.

Dr. Oscar Castillo was born in Vitoria, Spain, in 1974. He obtained his PhD from the University of the Basque Country in 2001, where he since then been an associate professor at the Faculty of Science and Technology. His current areas of interest include supramolecular recognition processes between nucleobases and metal-organic frameworks, design of 1D and 2D coordination compounds and their processability as nanomaterials, and magneto-structural correlations on coordination compounds containing aromatic bridging ligands.

Dr. Pablo J. Sanz Miguel was born in 1974 in Zaragoza, Spain. He obtained his Master's degree from the University of Zaragoza. He then joined Prof. Bernhard Lippert's group, completing his dissertation at the Technical University of Dortmund (Germany, 2005). He is currently working in a Juan de la Cierva post-doctoral position awarded by the Spanish Ministry of Science with Dr. Félix Zamora at the Universidad Autónoma de Madrid on nanomaterials.

Dr. David Olea was born in 1976 in San Sebastian, Spain. He obtained his physical-chemistry PhD from the Bordeaux I university, France, in 2004. He then joined Prof. Dr. Julio Gómez's group in the "New Microscopies" laboratory of the Universidad Autónoma de Madrid where he is currently working in a "Juan de La Cierva" post-doctoral position. His research interests are related to Atomic force microscopy imaging and nanotechnology; more precisely in the fields of conducting nanowires and supra-molecular assemblies.

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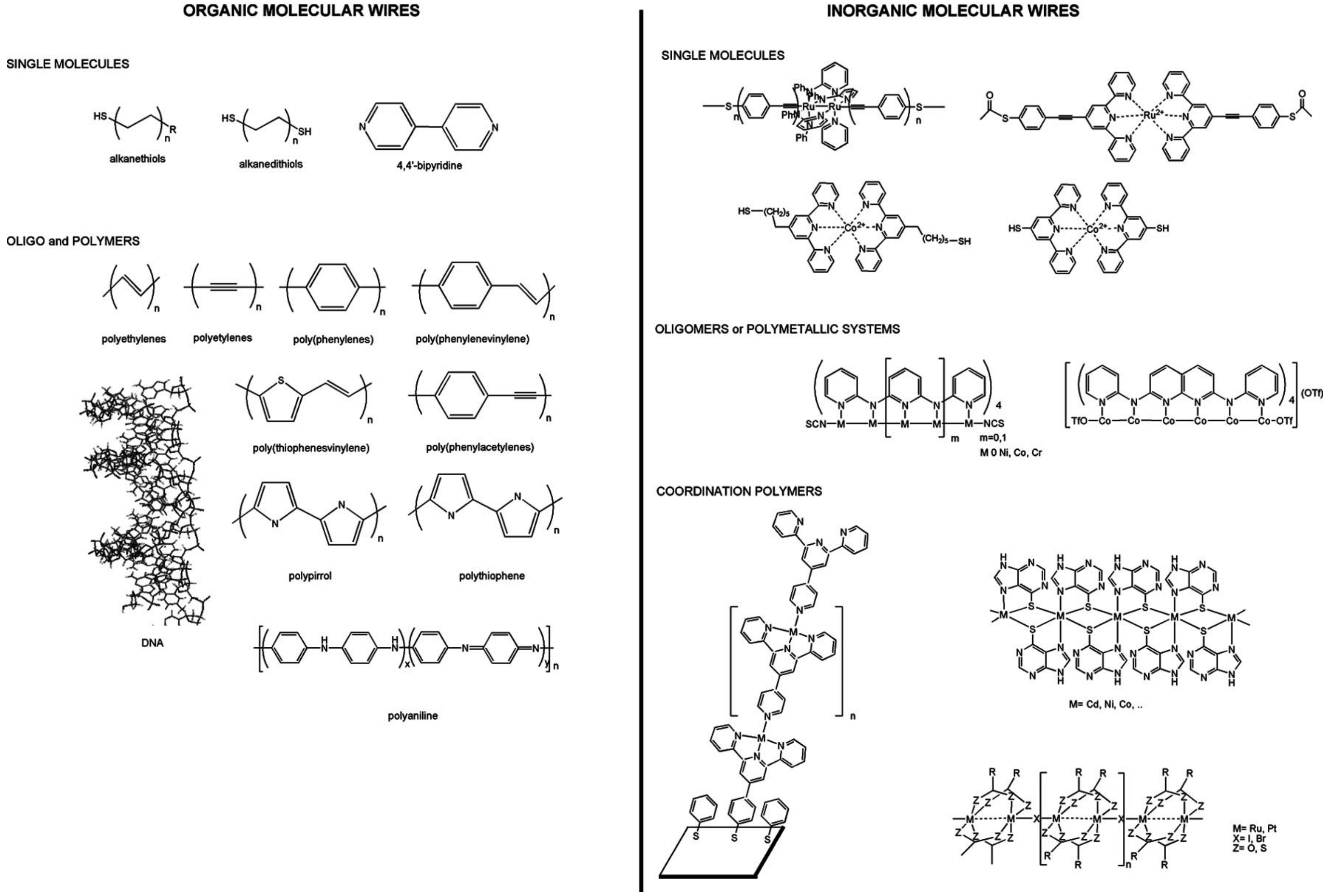
Dr. Félix Zamora was born in Cuenca (Spain) in 1967. He obtained his PhD in Inorganic Chemistry from the Universidad Autónoma de Madrid in 1994. Afterwards, he moved on to work with Prof. B. Lippert's group at the University of Dortmund (Germany) as a postdoctoral researcher. In 1996, he returned to the Department of Inorganic Chemistry (Universidad Autónoma de Madrid) as an Assistant Professor. Since 2002 he has been a full-time lecturer in the same Department. In 2004 he founded the "Nanomaterials" research group which is focused on the search for new nanomaterials based on inorganic systems. Special emphasis is devoted to the development of methods to organize coordination polymers on surfaces in order to characterize their electrical, magnetic and molecular-recognition properties by means of methods based on Atomic Force Microscopy.



Scheme 1. Summary of some selected systems studied as molecular wires.

dressed for several reasons, for instance the dependence of the current on molecule length and because length will play an important role in the construction of molecular devices.

The electrical conductivity measurements on a wide variety of single organic molecules (Scheme 1) show decay parameters β ranging from 1.5 to 0.04 Å^{-1}.[10] From these studies it seems clear that unsaturated π-bonded organic molecules increase conductivity at least at one order of magnitude.[10] However, few experiments have been performed to measure electrical conductivity across single inorganic molecules. The inorganic systems studied can be classified into: small molecules,[11,12] small oligomers[13] and coordination polymers[14] (Scheme 1). The β values observed for some metal-organic systems seem to improve the conductance of analogous organic molecules,[13] therefore the selective combination of metal ions with organic molecules to obtain *efficient* molecular wires seems to be of interest.[10]

The main scope of this minireview is to provide an overview on a novel branch of molecular wires based on coordination polymers. Coordination polymers are infinite aggregates of metal ions or fragments bridged by ligands. They self-assemble by coordination bonding in one, two or three dimensions to give a wide variety of structures.[15,16] The key to the design of a desirable polymer architecture is based on the suitable selection of the molecular building blocks, which also determine the properties of the resulting materials.[17,18] In recent years, research of these materials has increased exponentially, due to their current and potential applications. Among other functions, these compounds form porous materials and polymer magnets, and present chromism, nonlinear optical properties, redox properties and electrical conduction.[15,19] Specifically, herein we deal with aspects concerning the isolation of coordination polymers as single molecules on surfaces, since this is the first step for an accurate electrical characterization by means of conductive atomic force microscopy (C-AFM).

2. Some Methodological Notes

Before describing the advances made in the organization of diverse molecular wires, this section presents some essential methodology used in the isolation and characterization of single molecule chains on surfaces.

2.1 Scanning Probe Microscopy

Two microscopy techniques have mainly been used to characterize nanostructures adsorbed on surfaces: Scanning Tunnel Microscopy (STM)[20–24] and Atomic Force Microscopy (AFM).[25,26] Both scanning probe microscopies, STM and AFM, use a sharp probe moving over the surface of a sample.

In the case of STM, a bias voltage is applied to the metallic tip so that a tunnelling current flows below a very short distance between the tip and the sample (the tunnelling current decreases exponentially to the distance). Feedback is applied in order to maintain the tunnelling current constant, giving scanned images with possible atomic resolution.

In the case of AFM, the probe is a tip at the end of a cantilever. The raster scans are performed by a piezoelectric scanner. The cantilever deflections (and therefore the tip-substrate interactions) are monitored by a laser beam that is reflected off the rear site of the cantilever. Finally, the laser variations induced by the deflection of the cantilever are detected by a photodiode system. Two different modes are mainly used in AFM: contact mode and dynamic mode. In the first technique, the tip and the sample remain in short contact, while performing the scans. The drawback of this technique is that the tip induces high forces (in particular lateral forces) that could alter the scanned samples.[27] In dynamic mode, the AFM tip oscillates near its first resonance frequency (often hundreds of kilohertz) and is placed over the surface. In this case, the tip can also contact the sample, but with a much softer force, making this technique a better choice for scanning soft or poorly immobilized samples.

Typically, STM makes it possible to reach higher resolution on the *x* and *y* axes than AFM. The main drawback of this technique is the difficult sample preparation since it only works for very clean conductive surfaces and thus requires an extensive cleaning process. That is why STM has evolved over time into an ultra high vacuum technique. Besides, characterization of thin films can be a problem when they are poor conductors, imposing a maximum thickness for the film that critically depends on the decay factor β (for these films the current decay follows an exponential law with β being the exponential decay factor).[28] In contrast, any flat surface, regardless of its conductivity, is suitable for AFM measurements, and therefore it is not so dependent on the surface cleanness. Thus, AFM techniques allow, with a very simple sample preparation, determination of the height (*z* axis) of a 1D structure with a precision in the range of Ångstrøms, but resolution on the *x* and *y* axes is much less accurate and is determined by the final diameter of the tips, which can vary from 5 to 30 nm.

2.2 Physical Properties at Molecular Level

In this section, we define molecular level as measurements that refer to an individual molecule. The most extensive and powerful techniques for this approach are Scanning Probe Microscopies (SPM). Using this set of techniques it is possible to characterize the electrical conductance,[29] electrostatic interactions (electrostatic force microscopy, EFM[30]), local magnetic fields (magnetic force microscopy, MFM[31]) mechanical[32] and optical properties (near-field scanning optical microscopy, NSOM/SNOM[33]).

Conductivity studies of coordination polymers in bulk material (single crystals or powder) suggest, in some cases, the possible metallic or semi-conductive behaviour of the isolated chains.[34–36] However, it is essential to measure the electrical transport in individual polymers in order to test potential applications for nano-electronics.

In particular there are a variety of well-known methods to measure conductance across a single molecule. The experiments have been based on making a chemically modified electrode to establish the first molecule-electrode contact. The second electrode can be either a temporal contact (scanned prove) or a permanent contact (crossbar, sandwich). In addition it is possible to break the single electrode to measure those molecules trapped across the junction (break junction). Additionally, micro-fabrication techniques have approached the molecular scale. E-beam lithography is able to produce metallic electrodes with nanometer resolution (ca. 2 nm) which are suitable for trapping and measuring conductivity across molecules (nano-gap). Recently, an excellent review on this topic was published by Abruña.[37]

Conductance AFM can be used in two well defined geometries. In the first, there is a molecule carpet standing-up from a conductive substrate (in most cases a gold surface connected to the molecules through thiol groups). A conductive tip is used to image the surface and to obtain electrical characterization.[29]

The other geometry applies to long molecules lying on an insulated substrate. The surface is partially covered with a mask and then a gold electrode is evaporated leaving a sharp electrode edge.[38] When a polymer (both covalent and supramolecular polymer) is connected to the gold edge, direct measurement of its conductivity can be performed. The measurement is achieved by applying bias voltage between the electrode edge and a metallic AFM tip that is connected to the polymer. (Figure 1).[38] The vertical C-

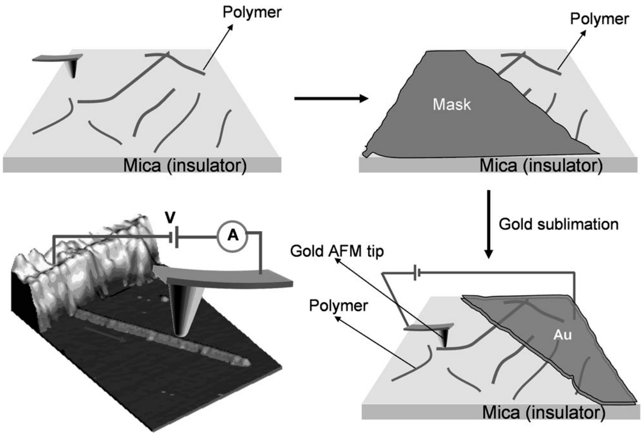


Figure 1. Schematic representation of the procedure to perform electrical measurements on molecules using the C-AFM technique in horizontal geometry.

AFM method is well suited for molecules that form thin films. However, it is always difficult to know the amount of molecules involved in the electrical contact. The second method can only be applied to molecules of a relatively long length ($>$ 100 nm) but it has the advantage that the molecule to be contacted can be clearly visualized before electrical characterization. Besides, the horizontal C-AFM method allows characterization of the resistance of the molecules as a function of their length. This is in fact the main advantage in the use of this technique, not only over the vertical geometry, but also over other techniques such as lithographically fabricated contacts and in situ measurements.[39,40]

On the other hand, the AFM tip can be used to manipulate the deposited entities. Thus, hard AFM tips are very useful in nano-indentation experiments for studying the mechanical properties of nanostructures.[14] For instance, deposition of individual chains on a surface offers the chance to obtain information about the mechanical properties of these fibers by comparison with other polymers. λ-DNA (used as reference polymer) was coadsorbed with individual chains of $[\mathrm{Cd}(6\text{-MP}^-)_2]_n$ (6-MP$^-$ = 6-mercaptopurinate). A force to cut first the DNA and then the polymer chains, using the same AFM tip, was applied. Since the tip was the same, the applied pressure for a given force (which was directly measured with the AFM) was also the same. By means of this approach we confirmed that individual chains of $[\mathrm{Cd}(6\text{-MP}^-)_2]_n$ are weaker than the λ-DNA strands as is to be expected for the cleavage of the coordination vs. covalent bonds.[14]

2.3 Adsorption Methods on Surfaces

Generally, coordination polymers are insoluble and this limited their processability by the common "wet" procedures typically employed in a chemical laboratory. Taking this drawback into account, a key factor for the nanotechnological applicability of coordination polymers is the development of efficient methods to isolate single-molecule entities on surfaces. One strategy is the extraction of single molecules from bulk samples, for which there is a need to overcome supramolecular cohesive interactions. This goal is reached by means of physico-chemical methods (such as sonication or sublimation) that provide enough energy to the system to remove the cohesion within the crystals, or by dissolution of the chains, which usually requires some chemical modification such as acid-base reactions (Figure 2). The methods developed in recent works following these principles are briefly reported below.

The sublimation of molecules has been widely employed to deposit organic compounds on surfaces.[41–43] Recently, it has also been shown to be a useful technique for working with coordination polymers. On 1D coordination polymers, the process starts with the rupture of the inter-chain and, later, intra-chain interactions, followed by adsorption of the small building blocks on the surface. At this point, the building blocks reassemble to regenerate the isolated chains in situ on the surface. A factor that should be considered to facilitate the reaction between the building blocks is the diffusion on the surface, which can be tuned by controlling the temperature. Sublimation methodology has been successfully applied to adsorption of 1D coordination polymers. Thus, compounds $\{[\mathrm{Co(ox)(Htr)_2}]\cdot 2\mathrm{H_2O}\}_n$ or $[\mathrm{Pt_2(dta)_4I}]_n$[44] have been characterized on Highly Oriented Pyrolytic Graphite (HOPG). In a related approach, Kern et al. sequentially deposited di- or tri-carboxylates and iron atoms by sublimation in an ultra-high-vacuum chamber. Reaction and subsequent assembly of these tectons resulted in formation of regular 2D structures.[45]

In addition, it has recently been reported that mechanical forces induced by ultrasound can induce cleavage of not only inter-chain, but also intra-chain interactions, as occurs by sublimation.[46] This has been widely verified for several coordination polymers.[47] Figure 3 summarizes the different processes that can be expected to occur when a 1D-coordination polymer is sonicated. Initially, a long chain can be cut into small activated fragments that later reorganize in solution or on the surface to generate circular structures or the initial linear molecules.

Another approach to generate the single chains of a coordination polymer from crystals is to chemically modify the terminal ligands of the polymer involved in the weak interactions among the chains. The reaction has to be able to remove these interactions but not to drastically change either the polymer architecture or its properties, as for example, protonation/deprotonation[48,49] of a ligand in a co-

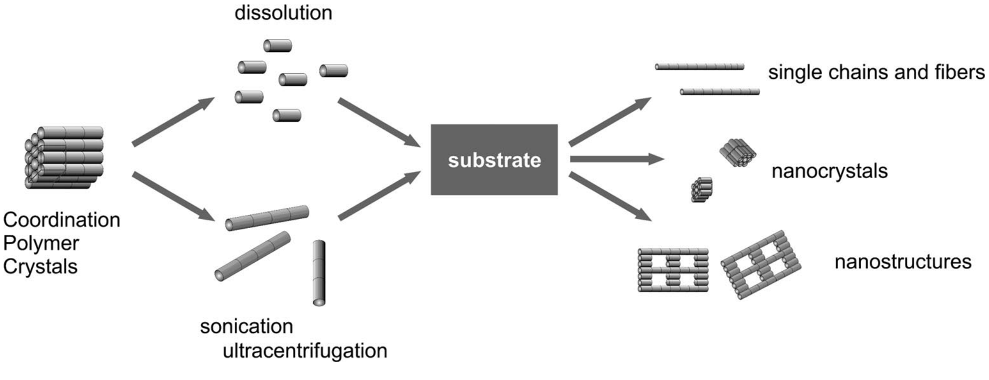


Figure 2. Scheme of different methods employed to form single polymers, fibers, nanostructures and nanocrystals in a surface.

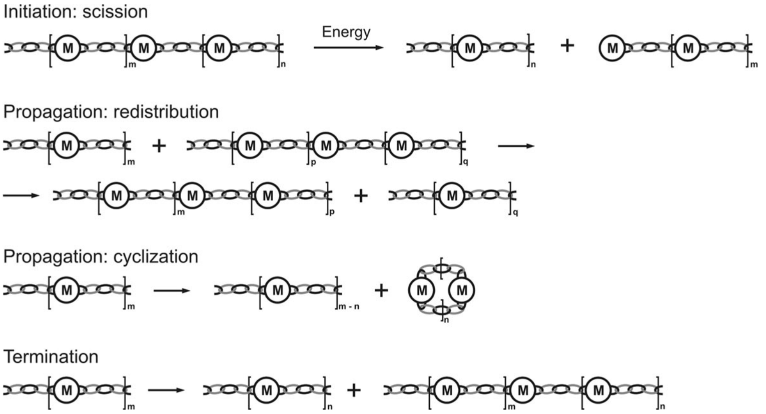


Figure 3. Elementary mechanism of the effect of ultrasound on a coordination polymer.

ordination polymer. The repulsion forces resulting from the charges induced from protonation/deprotonation processes, could be enough to release chains from the crystal.

Interaction with solvent molecules can also result in cleavage of coordination bonds in linear coordination polymers resulting in formation of small building blocks that are able to reassemble again. For instance, it has been reported that solubilization of ruthenium MMX polymers in ethanol leads to the formation of discrete solvated dimetallic species [RuRu(ethanol)]$^+$.[50] These saturated species can be activated by means of ultrasounds, which induce disruption of the weaker coordination bonds leading to unsaturated [RuRu]$^+$ and/or small oligomers in solution. It has been observed that these new activated species evolve in solution to generate long chains (Figure 3).[51] Moreover, a simple way to generate chains directly on the surface consists of inducing in situ reaction of the building blocks: metal ions and ligands. Applying this principle, by mixing diluted solutions of rigid linear organic coordinating tectons bearing two differentiated coordination poles with solutions of salts of suitable metal centers such as Co^{II} or Pd^{II}, resulted in isolation of 1D coordination networks on graphite surfaces.[52] Analogously, polymeric chains of zinc complexes of dipicolylglycyl (Dpg) peptides were prepared by deposition of highly diluted aqueous solutions on graphite.[22]

From recent reports, a new strategy can be envisaged to grow in situ coordination polymers of controlled dimensions that are vertically oriented with respect to the surface plane. First, the synthesis of 3D MOF $[Cu_3(BTC)_2(H_2O)]_n$ (BCT = 1,3,5-benzenetricarboxylic acid) has been recently achieved by sequentially combining the corresponding building blocks, growing a MOF structure in a step-by-step fashion.[53] The formation of the corresponding MOF was achieved by repeated immersion cycles of a functionalized surface, first in solution of metal precursor and subsequently in a solution of organic linker. Furthermore, in a very recent report, this method was applied to 1D structures, assembling metal ions by terpyridine-based ligands obtaining highly conductive molecular wires of lengths up to 40 nm.[54] Again, the assembly of the molecular wires was carried out via sequential coordination steps, by alternating immersions of the gold functionalized surfaces into a solution of Fe^{II} or Co^{II} salts and into a solution of a symmetric hexadentate ligand. These step-by-step cycles can be repeated as much as needed to control the length of a molecular wire, which is a significant advance towards the design of molecular circuits.

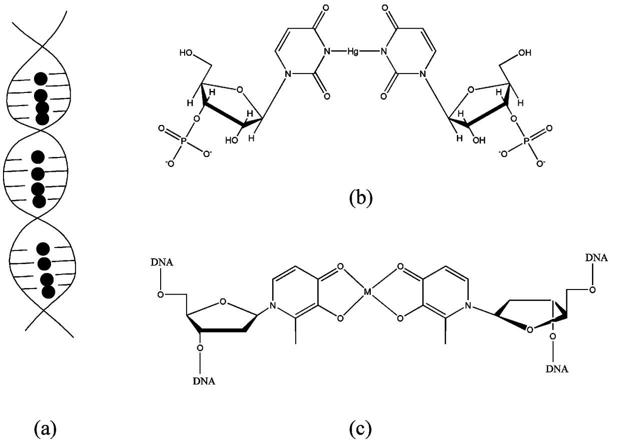
3. Advances in the Formation of Molecular Wires

3.1 From DNA to MOFs

DNA is a molecule of increasing importance in material sciences.[55] As a nanowire candidate, it presents an attractive chemistry that allows the formation of controlled architectures based on the sequence self-assembly.[4,56,57] However, its electrical characterization is still controversial. In fact, it has been described as anything from superconductor, conductor, semiconductor or insulator.[58] This wide range of results is probably related to the variety of parameters that can affect the final results such as DNA sequence,[59,60] DNA length,[58] DNA-surface interaction,[61] sample preparation and measuring technique,[7,62,63] and the nature of the electrical contacts between DNA and the macroscopic electrodes.[64,65] However, in all the cases in which DNA showed charge transfer behaviour, its length was less than 40 nm. It is currently widely accepted that it behaves as an insulator for chains of over 40 nm in length.[66] A detailed revision of the reasons why these parameters can affect conductivity measurements has been recently reported.[67] However, there is not a clear theoretical reason to believe that DNA should conduct electricity. It may certainly transport small density of current with an exponential decrease with the distance that is the case for all conjugated molecules.

Metal-coating of DNA has largely been used as an approach to produce metallic wires.[68] Essentially the idea is based on a simple process in which metal ions are added to a DNA solution in such a way that the ions exchange with the sodium ions of the sugar-phosphate backbone. Then the metal-ion-coated DNA is reduced with a chemical agent or light. Recently, a similar method has been used to generate uniform bimetallic wires of tuneable size by metallization of artificial DNA.[69]

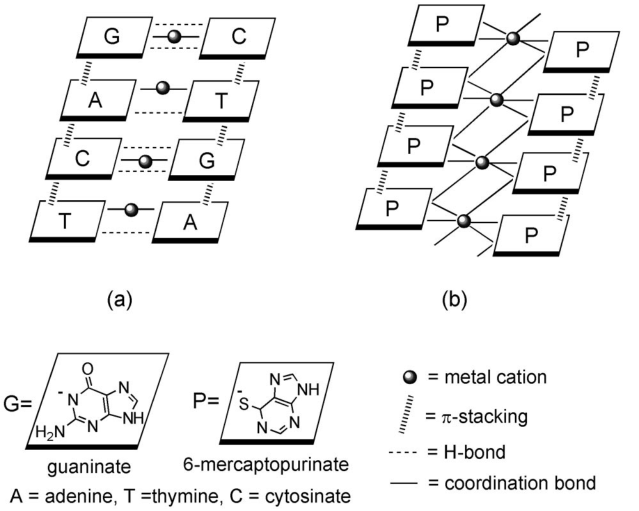
Several other approaches based on the modification of its electronic structure have been tried in order to increase conductivity on DNA.[70] One of these approaches is based on the insertion of metal ions in the duplex. Therefore, the metal ions are linearly stacked between the pair bases. This advance includes metal-ion-mediated base pairs with natural nucleosides[71–74] and metal-ion mediated base pairs with artificial nucleosides[75,76] (Scheme 2). An excellent overview focused on these studies has recently been published in this journal.[77]



Scheme 2. (a) Schematic representation of the concept; (b) a selected example[71] of metal-ion-mediated base pairs with natural nucleosides; and (c) a selected example[76] that includes metal-ion-mediated base pairs with artificial nucleosides.

A new candidate molecular wire based on a modified form of DNA, is the so-called M-DNA.[78] The initial structure proposed by Lee[78,79] consists of the substitution of the protons between guanine-cytosine and adenine-thymine by Zn^{II}, Ni^{II} or Co^{II} cations. It has been reported that this substitution is only achieved at high pH ($pH > 8$), at lower values this form reverses to DNA. However, the structure proposed by Lee is still unclear[80,81] since the exact position of the metal ions has not been determined. Moreover, aspects concerning its electrical characterization are controversial.[82,83]

In order to overcome the well-known problems concerning the restricted stability (just at high pH values), unclear structure and controversial electrical properties of the M-DNA, a simpler model has been investigated. This new approach is based on the selection of a 1D coordination polymer with a related structure to that proposed by Prof. Lee for M-DNA. A suitable model is the 1D-coordination polymer $[Cd(6\text{-}MP^-)_2]_n$ ($6\text{-}MP^-$ = 6-mercaptopurinate). The molecular structure of this polymer was well-established by X-ray diffraction.[84] Its structure, while preserving many of the features of M-DNA, is simpler and allows affordable theoretical modelling and experimental manipulation (Scheme 3). Thus, prompted by the idea of modelling M-DNA, investigation of this polymer represented the first step of a new path where the study of 1D coordination polymers deposited on surfaces has been revealed to be an outstanding field of research that is full of new challenges.



Scheme 3. Schematic representation of M-DNA structure suggested by Prof. Lee (a) and $[Cd(6\text{-}MP^-)_2]_n$ (b).

3.2 Mercaptopurine-Ligand-Based 1D Cadmium Coordination Polymers

The 6-mercaptopurine/cadmium system generates several related dimetallic and 1D polymeric compounds. Figure 4 provides a representation of the routes employed for the synthesis of the different Cd^{II} complexes with 6-mercaptopurine (6-MP).[49]

This system is highly pH-dependent, due to the non-, partial or total deprotonation of the two acidic hydrogens of the mercaptopurine molecule. In such a way, acidic pH values lead to dimeric complexes $[Cd_2(6\text{-}MP)_4(NO_3)_2](NO_3)_2$ (**1**) or $[Cd_2(6\text{-}MP)_4(H_2O)_2](NO_3)_4\cdot 2H_2O$ (**2**), depending on the solvent employed. pH values ranging between 4–5 lead to a 1D neutral coordination polymer $[Cd(6\text{-}MP^-)_2\cdot 2H_2O]_n$ (**4**). Finally addition of $Ca(OH)_2$ to a suspension of either complex $[Cd_2(6\text{-}MP)_4(NO_3)_2](NO_3)_2$ (**1**) or $[Cd_2(6\text{-}MP)_4(H_2O)_2](NO_3)_4\cdot 2H_2O$ (**2**), reaching up to pH 12, gives the 1D ionic coordination polymer $[Cd(6\text{-}MP^{2-})_2]_n\text{-}[Ca(H_2O)_6]_n$ (**3**), comprised of parallel packed $[Cd(6\text{-}MP^{2-})_2]_n^{2n-}$ polyanions and $[Ca(OH_2)_6]_n^{2n+}$ polycations, which are joined together by means of electrostatic interactions and hydrogen bonds.

The structure of these 1D chains is based on stacked $[Cd(6\text{-}MP^-/6\text{-}MP^{2-})_2]$ entities, which are linked through Cd–S bonds, forming a one-dimensional chain. The coordination mode of the mercaptopurine ligand in these polymeric complexes is similar to that reported for the bridging ligands in compounds **1** and **2**. However, a more detailed analysis shows a subtle but significant difference in the stacking of the *trans*-$[Cd(6\text{-}MP^-/6\text{-}MP^{2-})_2]$ subunits. The arrangement of the cadmium-mercaptopurine monomeric building blocks in compound **4**,[84] allows every mercap-

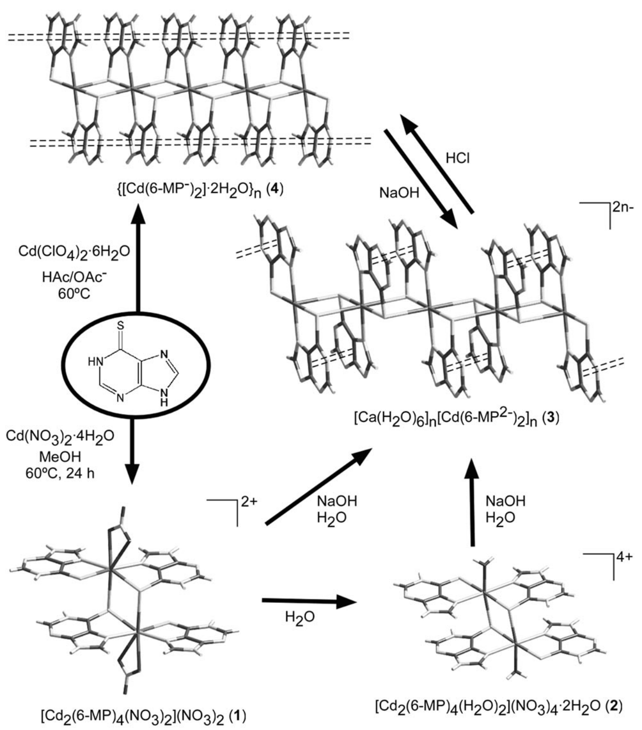


Figure 4. Synthetic routes of the 6-mercaptopurine/cadmium(II) system.

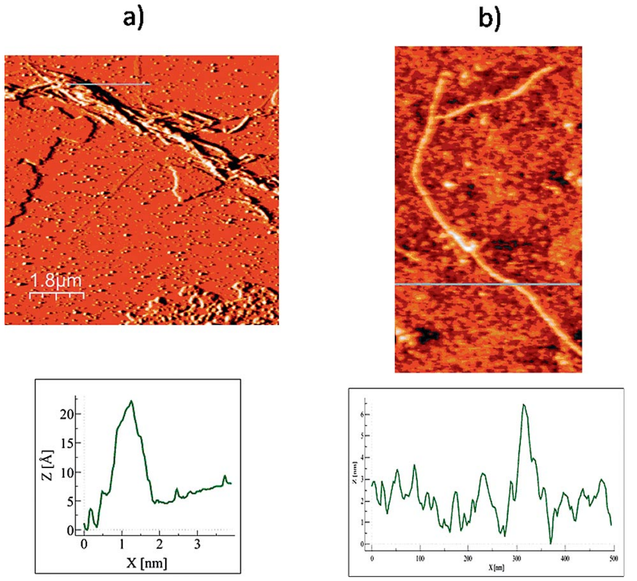


Figure 5. (a) High pass AFM filtered image showing the first stage of **4** processing after sonication (200 W, 40 kHz, 90 min) and soft centrifugation (8000 rpm, 10 min) and height profile of the nanocrystal. (b) AFM topography image of an individual polymer chain at the end of the treatment with sonication and prolonged centrifugation (8000 rpm, 20 min) and height profile across the molecule.

topurinate ligand to establish π-π interactions with the two adjacent ligands. In compound **3**, these interactions are hampered by the repulsive electrostatic force between the twofold deprotonated mercaptopurines, which leads to a chain arrangement that only allows π-π stacking with just one of the two adjacent mercaptopurinate ligands and even this stacking is weakened by a nonparallel divergent disposition [5.11(6)°]. The negative charge of the polymeric cadmium complex also leads to an increase in the metal–metal distance [4.139(1) Å for **3** vs. 3.918(3) Å for **4**].

The different methods used to get the single chains of these polymers isolated on surfaces from the bulk material are listed below.

Sonication: The crystal cohesiveness of $[Cd(6\text{-}MP^{-})_2\cdot 2H_2O]_n$ is ensured by means of hydrogen bonds between the chains which imply the crystallization of water molecules.[84] Therefore in order to weaken these intermolecular interactions a heating treatment was performed prior to sonication. It results in formation of the anhydrous coordination polymer, in which the chains are less tightly held together. Then, energy provided by sonication breaks the intermolecular interactions in addition to some of the coordination bonds, leading to chain fragments which can later reassemble to make longer chains but also in some cases rings formed by linking two ends of the chains. After sonication, the reaction media is a mixture of dispersed chains, nanocrystals, and fibers. Thus, centrifugation at high speed and long times only allows the lighter entities (i.e. single-molecule chains) to remain in the supernatant solution prior to deposition on mica (Figure 5).

Deprotonation: By treatment with NaOH it is possible to deprotonate the mercaptopurinate ligand of compound $[Cd(6\text{-}MP^{-})_2\cdot 2H_2O]_n$ affording the anionic polymeric complex found in **3**. As a consequence of the effects of the deprotonation on a crystal of **4**, where all the chains are neutral, the negative charge acquired by the chains will generate inter-chain repulsive forces, leading to a disaggregation of the new anionic polymeric chains. An AFM topography image shows a linear molecule of about 0.5 nm height (value in agreement with the X-ray height of a single polymer). This molecule is probably a single polyanion obtained by the complete deprotonation of **4**.

In situ Reaction: The reaction between the two building blocks of **4**, Cd^{II} and 6-MP, was carried out at low concentration on a highly oriented pyrolytic graphite (HOPG) surface. AFM images recorded immediately after solution deposition did not show organized structures. However, after heating the surface at 80 °C for 1 hour the AFM topography image shows fibrous structures with a height ranging from 0.5 to 5 nm, proving that in situ reaction leads to single polymers and fibers of **4**.[49]

Electrical properties of the isolated chains are the key for a potential application as molecular wires. Their electrical characterization was performed in a pioneering study dealing for the first time with the electric properties of isolated chains of a coordination polymer. Electrostatic force microscopy (EFM) and conductance AFM measurements indicate that these chains behave as insulators rather than molecular wires. Accordingly, DFT calculations indicate a large bandgap of 2.30 eV, small bandwidths (0.32 eV for the highest occupied molecular orbital, HOMO) and that the states with a large weight in the metal ions are low in energy, well below the Fermi level. Thus, the metal atoms do not behave as a conducting metallic wire, but rather as a chain of cations in an ionic compound. However, additional DFT calculations on $[M(6\text{-MP}^-)_2]_n$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II}) recently reported suggest that $[Cu(6\text{-MP}^-)_2]_n$ is a better candidate for molecular wire.[85]

3.3 $[Mn(\mu\text{-ox})(4atr)_2]_n$ (ox = oxalato; 4atr = 4-amino-1,2,4-triazole)

A different platform to obtain 1D systems is provided by oxalato bridging ligands. The nature of the structures formed from coordination of oxalate anions largely depends on the shape of the templating counterions and/or the features of the auxiliary ligands used to complete the metal coordination sphere. Thus, a wide variety of structures are observed as depicted in Figure 6. 1D complexes of formula $[M(\mu\text{-ox})(L)_x]_n$ can be obtained by using rigid ligands, such as pyridyl or triazole entities and even nucleobases, as monodentate terminal/axial ligands, which permit the polymerization process of the oxalato-metal framework.[86–88]

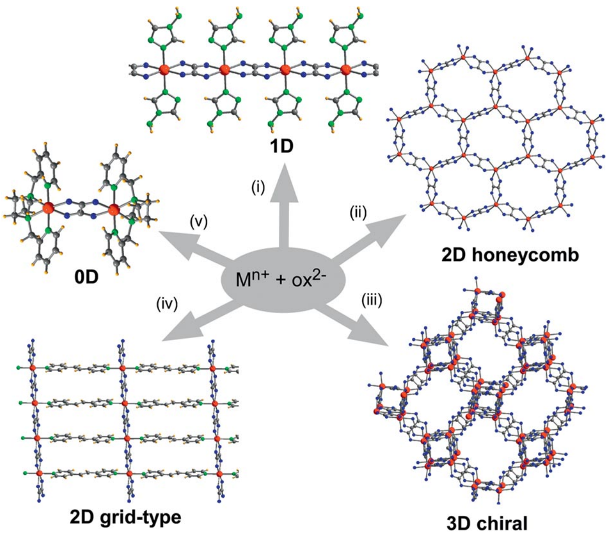


Figure 6. Tailoring of metal-oxalato frameworks using different organic ligands or templating counterions: (i) monodentate N-containing rings; (ii) achiral cations; (iii) chiral tris-chelated diimine cationic complexes; (iv) bidentate ligands such as 4,4′-bipyridine; (v) multidentate blocking N- or O-donor ligands.

The crystal structure of $[Mn(\mu\text{-ox})(4atr)_2]_n$ (**5**) consists of neutral linear one-dimensional chains in which *trans*-$[Mn(4atr)_2]^{2+}$ units are bridged by centrosymmetric bis-bidentate oxalato ligands, giving a distorted octahedral MnO_4N_2 chromophore (Figure 7).[48] The 1D chains run along the *a* axis and the terminal 4atr ligands are parallel to the propagation direction of the chain, due to a weak intramolecular hydrogen bond.

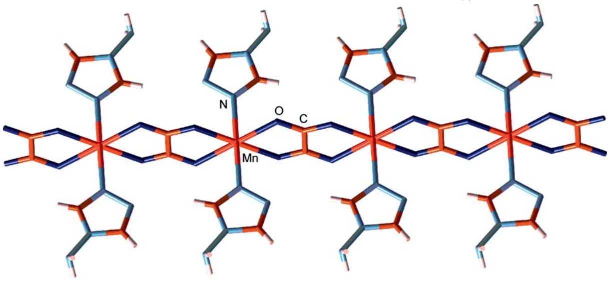


Figure 7. Lateral view of a polymeric chain of compound $[Mn(\mu\text{-ox})(4atr)_2]_n$.

In this case, sonication experiments were performed with special attention to the influence of the solvent and surface. Casting deposition on mica of a droplet from the solution obtained after sonication and ultracentrifugation of $[Mn(\mu\text{-ox})(4atr)_2]_n$ in ethanol leads to the formation of nanoparticles with an homogeneous height of 4 nm (Figure 8, a). These nanoparticles probably consist of chains curled-up from the polymeric complex. Thus, the final shape of the isolated chains is ruled by the relative strength of the intramolecular forces and the interactions with the substrate and with the solvent molecules. In contrast, adsorption of an ethanolic solution of **5** on a hydrophobic surface (HOPG) leads to formation of linear chains in high density (Figure 8, b). The height values range from 0.5 to 1 nm, which is in agreement with the expected diameter of a single polymer.[48] These results indicate that a key factor governing the shape of the isolated chains, in addition to the flexibility and characteristics of the polymeric complex, is the nature of the surface. As shown in Figure 8 (c), the molecule width is not uniform suggesting that more than one molecule is aggregated. A high resolution fast Fourier transform filtered STM image (Figure 8, d) shows parallel structures of the coordination polymer. This confirms the hypothesis of a multiple molecule structure for each chain observed in the AFM images.

Another possible method to obtain single chains of the polymer is deprotonation of the 4atr-coordinated ligands with a diluted solution of NaOH. Although a partial decomposition of the polymer is observed with subsequent formation of Mn_3O_4, the resulting solution deposited on mica led to single chains of **5** (Figure 8, e), of heights ranging from 0.4 to 0.6 nm, in good agreement with the expected diameter of the single chains from the X-ray crystal structure.[48]

3.4 MMX Chains

A unique case of particular interest to the search for long conducting molecules is the MMX family. Some MMX structures show metallic behavior in bulk samples, suggesting good perspectives for the use of some of these compounds as molecular wires. MMX structures consist of 1D chains built up from repeated halogen-bridged binuclear metal complexes, in which the two metal atoms of each bimetallic unit are linked pairwise by four ligands (Scheme 1).

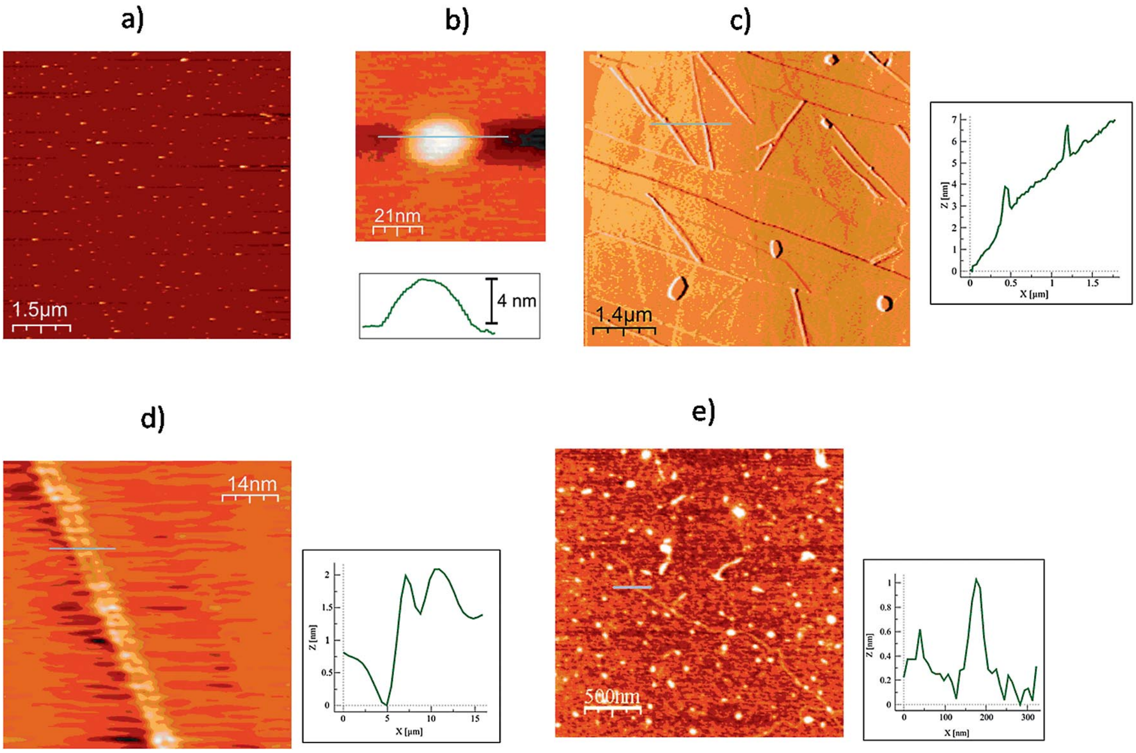


Figure 8. (a) AFM image of a homogeneous distribution of nanoparticles of compound **5** on mica. (b) AFM topography image of an individual nanoparticle with height profile. (c) High pass AFM filtered image of **5** deposited on HPOG showing a large number of chains with non uniform width. (d) High resolution STM topography showing the detail of the chains of (c). e) AFM topography image of single chains obtained after treatment of **5** with NaOH, centrifugation, and deposition on mica.

Compounds with this structure have been obtained using Platinum and Ruthenium metal centers. Deposition on surfaces of Ru-MMX has made it possible to observe interesting features on nanometric scale.

The structure of $[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$ consists of $[Ru_2(\mu\text{-}O_2CEt)_4]^+$ units connected by bromide ions to give linear chains. Accordingly, measurements of atomic force microscopy (AFM) of fibers deposited in mica gave evidence of 1D entities of lengths from 0.5 to 5 µm and a height of ca. 0.7 nm. However, when the same MMX compound was deposited on a graphite surface, only helical bundles were detected. A more detailed analysis by means of high-resolution scanning tunneling microscopy (STM) revealed that the chains exhibit helical structures with various helix periodicities, chiralities and diameters.[89] The formation of helical superstructures suggests that in graphite, the formation of intermolecular interactions costs less energy than the binding to the surface.

Another interesting feature was found for the MMX of formula $[Ru_2I(\mu\text{-}O_2CEt)_4]_n$. AFM topographies were different depending on the time allowed in solution after sonication. The image of a solution of complex immediately deposited after sonication shows dispersed structures of undefined shape. If the sonicated solution was allowed to stand for one hour before adsorption on the mica, the corresponding AFM image shows a random distribution of ring like structures of a much higher definition. One day after sonication deposition of the solution on mica results in the observation of irregular linear structures of highly irregular heights. However, 19 days after sonication the solution evolves in such a way that the deposited material presents well defined, but not perfect, linear structures. After 43 days, well defined micron-length wires of a uniform diameter of ca. 0.5 to 1 nm were observed.[51]

The fact that the MMX of formula $[Pt_2(\mu\text{-}CH_3CS_2)_4I]_n$ shows a metallic conductivity in crystalline phase at room temperature prompted a detailed theoretical analysis of its structural and electronic properties. The results obtained indicate that single chains with the uniform structure $M^{2.5+}–M^{2.5+}–X–M^{2.5+}–M^{2.5+}–X$, which is the phase observed at room temperature by X-ray diffraction, has a very robust metallic behaviour that is in agreement with the experimental findings. This outstanding conductivity can be understood by this theoretical work regarding the fact that the metallic *M* band that characterizes the system is the result of simultaneous hybridization of metal orbitals with the halogen and with the dithioacid ligands.[90] These results suggest that MMX are good candidates for use as molecular wires, and experimental work is in progress to isolate single molecule chains of Pt MMX and perform their electrical characterization.

4. Conclusions

The emergent area of nanotechnology requires new procedures to organize materials on nanometer scale.[1] Specifically, the construction of nanocircuits based on molecules will require conductive molecules and the capability to organize them. To this end, DNA has been considered a molecule of major interest. However, to date, isolated single chains of DNA longer than 40 nm have shown insulator behaviour. To overcome this drawback, early work with 1D MOFs as molecular wires has been performed. However, despite the electrical characterization of the first isolated individual chains showing insulator behaviour, recent results suggest that suitable metal-organic frameworks can be excellent candidates for conductive molecular wires. Moreover, these seminal works have developed new techniques to organize on molecular scale 1D coordination polymers on surfaces. These are based on the separation of the individual chains from the microcrystal of the bulk sample and/or in situ reactions of the corresponding tectons. The disaggregation can be achieved by simple physical methods such as sonication-centrifugation-deposition and by direct sublimation-deposition of the bulk material. Chemical treatments, which are based on the characteristics of the coordination polymer, such as protonation/deprotonation or solvation can also be employed successfully to disperse the individual chains from the bulk sample. Thus, a new landscape has appeared in front of us. The search for new candidates of molecular wires within diverse families of 1D polymeric coordination compounds is wide open.[85] In fact, recent DFT calculations have indicated MMX chains as good candidates and future theoretical work will probably direct the design of new MOFs with suitable electrical properties.[90] The formation of 1D nanostructures of coordination polymers is essential in the search for potential nanotechnological applications.

The organization in complex structures of molecular wires based on coordination polymers can probably be achieved through the suitable functionalization of the terminal ligands in such a way that they can interact via H-bonding with DNA-nanoarrays. Therefore, DNA will act as the template for these new molecular wires allowing construction of nanocircuits. This microreview presents a very young area of research and so further studies will surely appear in order to obtain a deeper understanding of the factors that direct the organization of the 1D nanostructures of coordination polymers on the surfaces.

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