MMX polymer chains on surfaces†

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Fibres of $[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$ polymer have been isolated on different surfaces under specific conditions, and morphologically characterised by AFM and STM, showing an unexpected helical internal structure.

Coordination polymers and extended inorganic–organic hybrid materials have attracted much attention in the development of new functional materials due to their interesting physical and chemical properties.[1,2] However, controlled assembly of these materials on solid surfaces has been very little explored; nano-functionalized surfaces with metal–organic polymers may present properties such as molecular organization and host–guest recognition.[3] Recently, highly ordered metal ion arrays have been suggested to be used in molecular information storage and processing devices.[4–6] A relevant subgroup of those coordination polymers are the so-called MMX polymers. These 1D halogen-bridged mixed-valence compounds are comprised of two metallic centres linked by organic ligands, usually carboxylates or dithiocarboxylates, that facilitate short metal–metal distances, and a halides acting as bridging ligands between the dimetallics subunits. They have extensively been investigated in the last few years because their physical properties, in particular those containing ruthenium and platinum.[7–19]

In this work we have synthesized and characterized by X-ray diffraction‡ the MMX polymer $[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$ (**1**). Its structure, with crystallographically imposed 4/*m* symmetry, shows two Ru atoms linked by four propionate bridging groups with the axial positions occupied by bromide ligands. The Ru–Ru distance is 2.2880(9) Å. This distance is comparable with those found in the polymers $[Ru_2Br(\mu\text{-}O_2CR)_4]_n$ described elsewhere[20,21] [R = H, 2.2897(7) and R = Ph, 2.2906(7) Å]. The structure of **1** (Fig. 1) consists of $[Ru_2(\mu\text{-}O_2CEt)_4]^+$ units connected by bromide ions to give linear chains (Ru–Br–Ru angle = 180.0°). These linear chains are in contrast with the formation of zigzag arrangements in $[Ru_2Br(\mu\text{-}O_2CH)_4]_n$ and $[Ru_2Br(\mu\text{-}O_2CPh)_4]_n$. The Ru–Br–Ru angles in these compounds are 109.99(3) and 117.00(3)°, respectively. Interchain interactions in **1** are restricted to van der Waals forces. The diameter of the chains in **1** is about 7 Å (Fig. 1 right).

As in other RuRuX compounds, **1** presents interesting magnetic properties. This fact gives an added value to this polymer in material science. We have measured the μ_{eff} value to be 3.60 μ_B at 300 K. This corresponds to the presence of three unpaired electrons in accordance with the $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ ground state configuration.[22] The representation of the magnetic susceptibility versus temperature shows a maximum at 31 K indicating a strong antiferromagnetic coupling between the diruthenium(II,III) units. The magnetic data of **1** has been fitted using a model[9] that considers a strong antiferromagnetic coupling ($zJ = -8.9$ cm^{-1}) and a large zero-field splitting ($D = 89$ cm^{-1}) (ESI,† Fig. S1).

A current central focus of the research in coordination polymers is the formation of elementary structures of these supramolecules on substrate surfaces and their characterization by high-resolution microscopy techniques.[3,23–27] These techniques can be also used to study RuRuX polymers on surfaces. Structural data reported on RuRuX polymers indicate that the Ru–X–Ru angles are flexible,[7,8,18,19] hence, in addition to linear chains, more complex organizations can be formed when adsorbing these polymers on substrates. Solubilization of RuRuX leads to $[RuRu]^+$ and X^-.[28,29] Self-assembly of these two building blocks from solution could lead to organizations on surfaces.

Casting deposition of solutions of compound **1** in aqueous sodium dodecyl sulfate (SDS), 0.01 wt% (5×10^{-1} mg mL^{-1}) adsorbed on mica leads to the formation of fibres of compound **1**. Fig. 2 shows an atomic force microscopy (AFM) topography image of two homogeneous fibres with a height of *ca.* 0.7 nm.[30] This value is in good agreement with that obtained by X-ray diffraction for individual polymer chains. To our knowledge this is the first time that those structures have been observed for MMX polymers. As stated above, the formation of fibres probably take place after complete solubilization of **1** (assisted by sonication) and self-recognition of the $RuRu^+$ and Br^- subunits. AFM images reveal a high surface concentration of the molecules on mica which supports a good yield of the process. Fig. 2(c) shows a statistic of the molecule lengths, proving that the fibres formed have lengths from 0.5 to 5 μm. Therefore, the method applied is suitable to produce nanowires of single MMX chains.

Since we have already observed an important effect of the surfaces on the organization of coordination polymers[23,24] **1** was adsorbed on highly oriented pyrolitic graphite (HOPG), a substrate with completely different physical chemistry properties than mica. Large-scale AFM images show fibres of different diameter and lengths which are very often, but not always, located along graphite steps. Fig. 3(a) right shows a high-resolution scanning tunnelling microscopy (STM) image fibre structures

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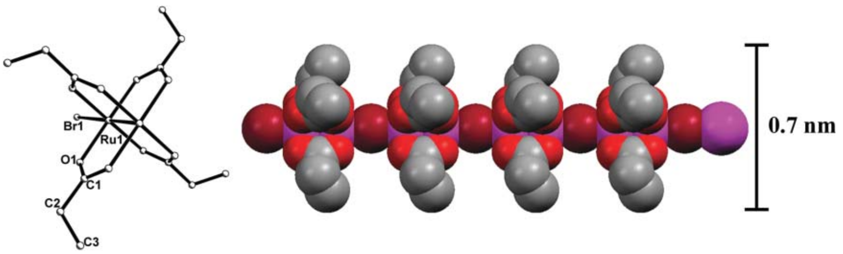

Fig. 1 PLUTO view of the $[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$ (left, the hydrogen atoms and the disorder of the methyl groups are omitted for clarity) and space fill representation of one chain (right).

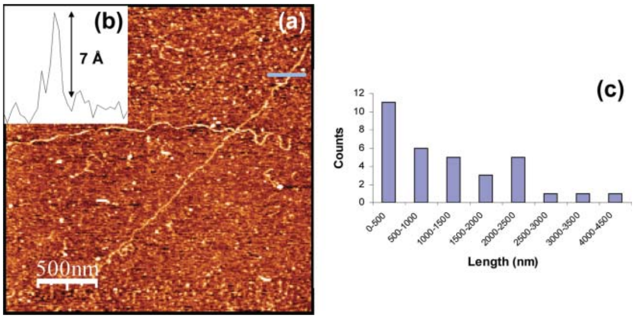

Fig. 2 AFM topography image (a) and height profile across the line (b) of a single chain of the $[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$ polymer (5×10^{-1} mg mL^{-1} water–SDS (0.01 wt%)) adsorbed on mica. (c) Number of molecules *vs.* molecule length for $[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$.

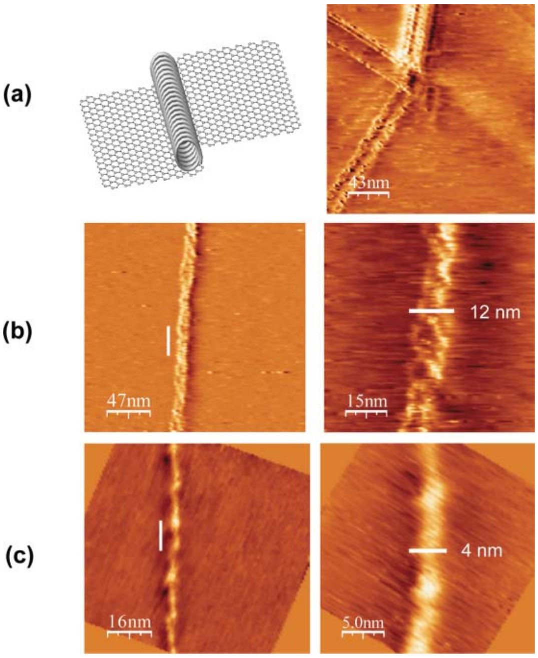

Fig. 3 (a) Cartoon representation of a polymer helical bundle adsorbed on a graphite step (left). STM topography image showing wires adsorbed on the edges (right). (b) High pass filtered STM topography image of an isolated wire (left) and STM topography zoomed image of the former (right). (c) STM topography image of a thinner wire (left) and zoomed area of the former (right).

adsorbed along a graphite steps. This preference for the HOPG defects was already reported[24,27] and explained as a consequence of the higher stabilization provide respect to the flat substrate. In addition to the structures formed along the steps, we have also observed fibres on flat terraces. The STM images, with atomic periodicity resolution, show that in the case of isolated fibres adsorbed on flat regions, the direction of the fibres follows the general directions of graphite atomic rows (ESI,† Fig. S2). This result suggests that the graphite rows act as templates for the fibres adsorption. As can be seen in Fig. 3(a), the fibres exhibit different diameters with complex internal structure. STM images of isolated fibres provide an explanation for this observation. Fig. 3(b) and (c) reveal that the chains exhibit helical structures with different helix periodicity, chirality and different diameters as already reported for other polymers.[27,31] Fig. 3(b) portrays an open double stranded right handed helix (the chirality of the helices was determined according to Ohira *et al.*[32]) with a periodicity of 25 nm (vertical bar in Fig. 3(b) left) and a width of ~12 nm. Each strand width is about 3.5 nm. According with the X-ray data this would be in good agreement with the expected width for a 4–6 single polymer bundle. Left-handed helices were also found, as shown in Fig. 3(c). This helix exhibits a smaller diameter of 4 nm and a periodicity of 9 nm (vertical bar in Fig. 3(c) left). In this case the strands are close packed and it is not possible to distinguish them. One can make the hypothesis that the higher helical fibres (like in Fig. 3(b)) are composed of other smaller helices like the one shown in Fig. 3(c). Especially if one remarks the little dots in the strands of the helix in Fig. 3(b) that suggest again, the helicity of these strands. On the contrary, nothing can be said about the composition of the strands of the smaller fibres since the resolution of the images does not provide enough information. Fig. 3(a) left depicts a schematic drawing illustrating the situation described above. No single molecules were found on the graphite substrate. Helical bundles were only observed, suggesting that the intermolecular affinity is higher that the one with the HOPG surface. The formation of helical superstructures could be explained in terms of binding energy minimization: forming intermolecular interactions costs less energy than binding to the graphite surface. Furthermore, the unexpected chirality induced by the helix structure (the chains do not present any chiral atom) can be explained by the decrease of contact area between the molecule and the graphite provided by these types of geometrical conformation.

As commented above the interesting physical properties of MMX polymers in solid state, especially those related with conductivity and magnetism, make this one-dimensional material very appealing for technological applications. All the previous studies have been restricted to the macroscopic scale in the solid state. In this work we have demonstrated the possibility to create one-dimensional structures of these polymers by controlling the solution and adsorption conditions. These results may allow extending the applications of MMX compounds as potential molecular wires with very promising magnetic properties. Work on physical properties of the isolated single chains of $[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$ and other MMX polymers are currently undergoing.

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Notes and references

‡ *Crystallographic data* for **1**: $C_{12}H_{20}BrO_8Ru_2$, M_r = 574.33, crystal size 0.10 × 0.13 × 0.32 mm, tetragonal, space group $I4/m$, a = 11.0008(7), b = 11.0008(7), c = 7.7052(7) Å, V = 932.46(12) Å^3, Z = 2, D_c = 2.046 g cm^{-3}, $F(000)$ = 558, μ = 3.794 mm^{-1}, 617 independent reflections (R_{int}= 0.0964), R_1 ($I > 2\sigma(I)$) = 0.0265, wR_2 (all data) = 0.0677.

Representative crystals were mounted on a Bruker Smart-CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation. Data were collected, at 296(2) K, over a hemisphere of the reciprocal space by a combination of three exposure sets. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS and SHELXL programs.[33] CCDC 284750. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613836e

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