

Time-Dependence Structures of Coordination Network Wires in Solution

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Coordination polymers are infinite aggregates of metal ions bridged by ligands. They self-assemble by coordination bonding in one, two, or three dimensions.¹ MMX polymers are a particular type of coordination polymers formed by dimetallic subunits bridged by halides (Cl, Br, or I). MMX polymers are synthesized as one-dimensional chains that interact between them to form a three-dimensional crystal. The key to designing interesting coordination polymer architectures is the selection of suitable molecular building blocks, which also determine the properties of the resulting materials. Coordination polymers, in particular MMX, are very appealing because of their chemical–physical properties such as magnetism,^{2,3} electrical conduction,^{4–6} chromism,^{7,8} and nonlinear optics⁹ and because of appealing applications as, for instance, porous materials,^{1,10–12} colloidal particles,¹³ etc. However, the use of these compounds in many fields is usually limited by their restricted processability, as a consequence of their lack of solubility, rapid degradation in solution, and, in some cases, decomposition upon heating.¹⁴ Consequently, coordination polymers are difficult to process as films, fibers, or other objects of desired shape. In this regard, the most successful methods reported so far are sublimation of the building blocks,^{15,16} self-assembly of selected building blocks (metal and ligands),¹⁷ and ultrasonication of coordination polymers. Using this former procedure, linear chains of coordination polymers have been isolated on surfaces and characterized by atomic force microscopy (AFM).^{18–20}

Besides the already mentioned properties, reversibility is a relevant feature that differentiates coordination polymers with respect to classical covalent polymers.^{21,22}

ABSTRACT We present a mechanochemistry-based procedure to isolate individual chains on surfaces of a ruthenium MMX polymer. After sonication of solutions containing the two building blocks of the mentioned MMX polymer, time-depending structures are formed in the solution. The architecture of the different structures obtained in this process, as a function of the time, is monitored using atomic force microscopy. The resulting structures exhibit uniform subnanometer diameters over microns length, in agreement with the expected diameter for an individual polymer chain. From the atomic force microscope images, we infer a long persistence length for the linear structures. Finally, the effect of the temperature solution in the formation of the different structures is also addressed.

KEYWORDS: self-assembly · supramolecular chemistry · nanostructures · coordination polymers · mechanochemistry

Reversibility is a direct consequence of the metal–ligand coordination bonds that can be broken by physical methods (thermal, mechanical forces, etc.). In particular, the use of ultrasound has been proven to be a suitable source for the scission of the metal–ligand bonds of coordination polymers. A recent work reported on the dynamics in solution of a Pd^{II}-based coordination polymer.²³ According to this work, the result of ultrasonication of the polymers is to induce breakage of their chains in homogeneous solution. The polymer fragments evolve with time in solution in a reversible way forming first small oligomers (linear and circular) and then long linear chains. This is one of the very few examples of studies in solution on coordination polymers. However, essential aspects concerning structural features, such as architectures of the species present in solution and their evolution, are still poorly described. In this work, we use the ability of ultrasound to induce breakage of coordination bonds to produce activated species which evolve by self-recognition to form with time different one-dimensional architectures in solution that have been observed by means of AFM

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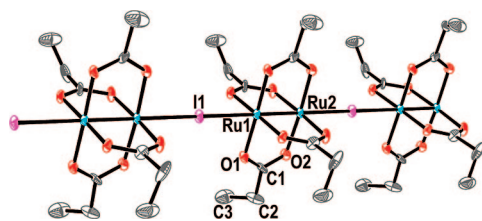


Figure 1. ORTEP view of a chain of $[\text{Ru}_2\text{I}(\mu\text{-O}_2\text{Cet})_4]_n$ (**1**) showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

measurements after deposition on surfaces. This procedure is shown to be a suitable tool to produce long individual one-dimensional chains with subnanometer diameter.

RESULTS AND DISCUSSION

The polymer $[\text{Ru}_2\text{I}(\mu\text{-O}_2\text{Cet})_4]_n$ (**1**) is synthesized in a similar way to that previously reported.²⁴ The conductivity measurements of **1** in methanol solution (*ca.* 10^{-3} M, $90 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) indicate that this compound behaves as a 1:1 electrolyte in this solvent,²⁵ and therefore, the Ru–I bond is broken giving $[\text{Ru}_2(\mu\text{-O}_2\text{Cet})_4]^+$ and I^- ions. Suitable crystals of **1** for X-ray diffraction analysis were isolated by slow evaporation from a methanol solution. The structure consists of $[\text{Ru}_2(\mu\text{-O}_2\text{Cet})_4]^+$ units connected by iodide ions giving a linear chain. The linear chains of **1** are interconnected by van der Waals forces. The dinuclear unit has two ruthenium atoms linked by four propionate ligands with the axial positions occupied by the bridging iodine ions. Figure 1 shows an ORTEP view of one chain

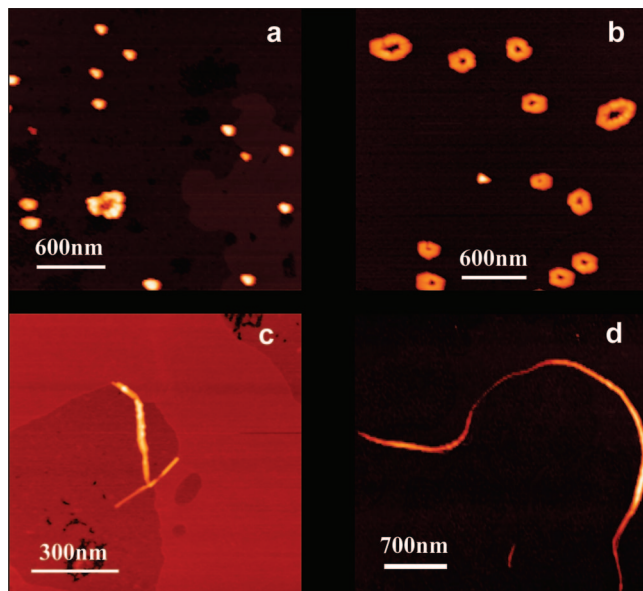


Figure 2. AFM topographies showing the evolution of **1** in ethanol solution after sample adsorption on a mica substrate: (a) time = 0, the image shows dispersed structures with ill defined shape; (b) time = 1 h, the image shows a random distribution of ring-like structures with a much higher definition in (a); (c) time = 1 day, the rings evolve to irregular linear structures with very irregular heights; (d) time = 19 days, the image shows well defined, but not perfect, linear structures.

TABLE 1. Selected Bond Lengths and Bond Angles for $[\text{Ru}_2\text{I}(\mu\text{-O}_2\text{Cet})_4]_n$ (**1**)^a

bond lengths (Å)		bond angles (deg)	
Ru(1)–Ru(2)	2.288(2)	Ru(2)–Ru(1)–I(1)	180.000(1)
Ru(1)–I(1)	2.851(6)	Ru(1)–I(1)–Ru(2)#1	180.0
Ru(2)–I(1)#5	2.905(6)	O(1)–Ru(1)–Ru(2)	90.9(4)
Ru(1)–O(1)	2.017(11)	O(2)–Ru(2)–Ru(1)	87.6(3)
Ru(2)–O(2)	2.049(13)		

^aSymmetry transformations used to generate equivalent atoms: #1 $x, y, z + 1$; #2 $-x, -y, z$; #3 $y, -x, z$; #4 $-y, x, z$; #5 $x, y, z - 1$.

of **1**. Table 1 provides selected bond distances and angles of the complex. The coordination polyhedron of the ruthenium atoms are distorted with respect to regular octahedral arrangements. The Ru–Ru distance of 2.288(2) Å and the other bond distances and angles in the diruthenium unit are similar to those reported in related compounds. The linearity of the chain is defined by the Ru–I–Ru angle of 180.0°. Magnetic measurements on complex **1** at room temperature shows a magnetic moment of 3.81 μ_B in accordance with the $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ ground-state configuration proposed by Norman *et al.*²⁶ The variation of the magnetic susceptibility with temperature shows a maximum at *ca.* 30 K. A similar maximum and an analogous paramagnetic tail have been observed previously in all diruthenium(II,III) complexes with linear chains. This maximum is attributed to a strong antiferromagnetic coupling between the diruthenium(II,III) units through iodine atoms (see the Supporting Information).

Crystals of **1** were dissolved in ethanol and sonicated for 2 h at 30 °C. Ten microliters of a diluted solution (3×10^{-6} g/L) was deposited on a mica substrate and left to dry. AFM images were acquired in dynamic mode using a Nanotec Electronica system and processed using WSxM.²⁷ The solution was stored at 20 °C, and the adsorption procedure and AFM characterization were again performed at various successive times, within a period of 53 days.

AFM images taken on a mica surface where a droplet of a solution of **1** was deposited immediately after polymer sonication ($t = 0$) show dispersed structures with undefined shape (Figure 2a) that we take as an indication of low organization of small pieces of 1D oligomer formation in solution. The basic assumption is that the AFM images provide a frozen picture of the species in solution as it has been reported for DNA.²⁸ Once the structures are observed on the surface, they do not experience any further evolution other than trivial contamination by the surrounding atmosphere. One hour after the solution of **1** was sonicated and allowed to stay at 20 °C, the solution underwent evolution as can be verified in the AFM images of a droplet adsorbed on mica (Figure 2b), in which a random distribution of ring-like structures with a much higher definition than in the $t = 0$ image is shown. The rings have a typical diameter of about 270 ± 27 nm and a height

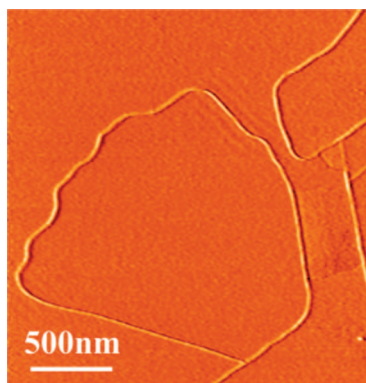


Figure 3. AFM topographies showing well defined wires with a uniform diameter of ca. 0.5 to 1 nm obtained from a droplet deposited on mica of solutions of **1**, 43 days after sonication.

of 11.6 ± 0.8 nm. The evolution of these structures in solution is clearly observed by adsorption on a mica surface of a solution of **1**, 24 h after sonication ($t = 24$ h). Formation of rings evolves to irregular linear structures (Figure 2c) with non-uniform height presenting, in many cases, irregular clusters at one or both ends. The typical length of the structures is about 400 nm. When the sonicated solution of **1** stays at 20 °C for 19 days and a droplet is deposited on a mica surface, well defined

linear structures, wires, can be observed (Figure 2d). The average wire length is now about 1 μm , but some of the structures can be as long as 4 μm . The diameter of the wires is still not perfectly uniform ranging between 2 and 12 nm.

Finally, AFM images (Figure 3) taken from a droplet deposited on mica of solutions of **1**, 43 days after sonication ($t = 43$ days), show well defined wires with a uniform diameter of about 0.5 to 1 nm. This smaller diameter is expected for one or few individual chains of **1**. The length of the wires ranges from 2 to 8 μm , indicating the formation of long one-dimensional wires in solution.

Figure 4 provides a feasible schematic interpretation of the dynamic process. In a first step, nonsonicated solution of **1** in ethanol gives a mixture of two species: $[\text{SRuRuS}]^+$ ($\text{S} = \text{ethanol}$) and I^- .^{29,30} Deposition on a mica of this solution leads to homogeneous layers with islands (Figure 5). Ultrasonication of the initial solution induces mechanical scission of Ru–ethanol bonds (the weaker bonds) and, therefore, formation of activated coordinatively unsaturated species $[\text{RuRu}]^+$ which easily self-assemble with I^- forming oligomers $[\text{RuRu}]_m$.²³ The size of these oligomers increases with time since they present reactive stick-ends. Finally, this

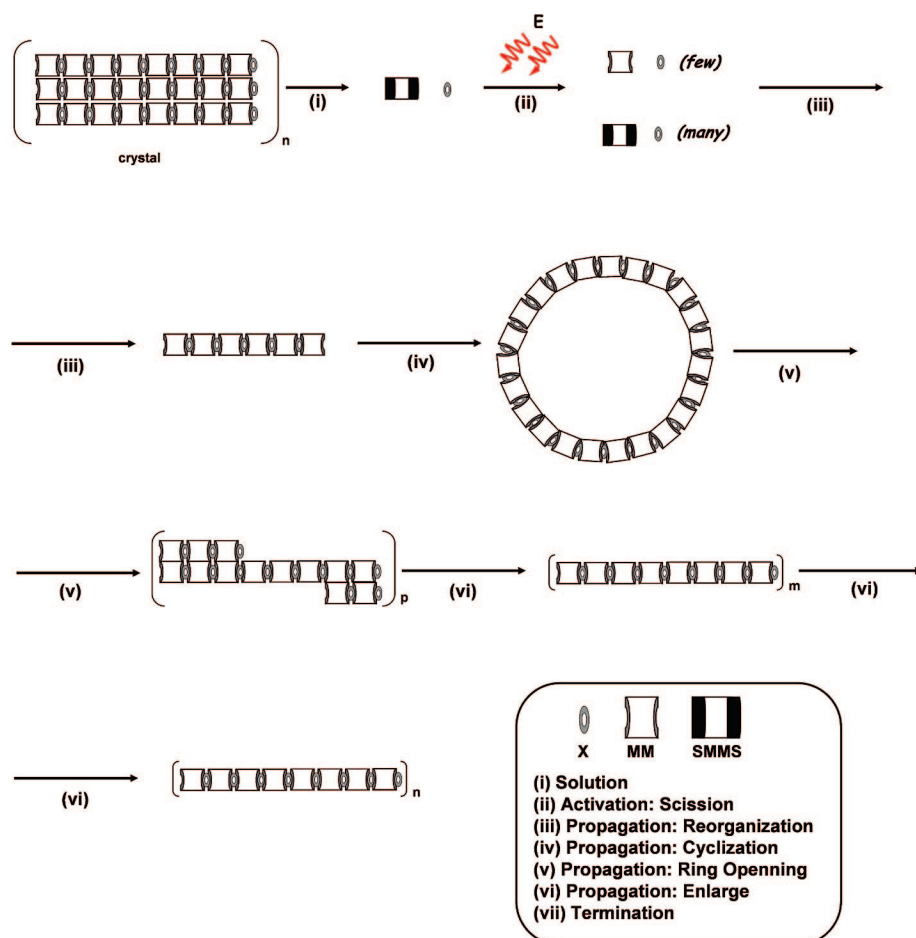


Figure 4. Proposed steps of the evolution in solution of **1** after solution and sonication in ethanol.

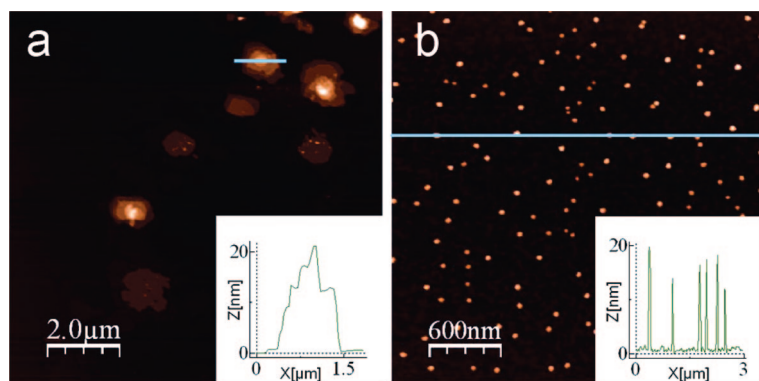


Figure 5. (a) AFM topographies of nonsonicated ethanol solution of **1**. (b) Evolution of the substrate structure shown in (a) after heating at 80 °C for 1 h. The islands collapse to small clusters of 12–14 nm height. The insets shown in (a) and (b) are cross sections along the corresponding lines.

process leads to formation of very long $[\text{RuRu}]_n$ ($n > m$) chains. It should be noticed that, in an intermediate step, the chains of the oligomers are closed to form rings. This is attributed to the formation of intramolecular coordinative bonds between unsaturated stick-ends of the same oligomer. This fact has been already described for coordination polymers^{23,31} and classical linear polymers.³²

In order to obtain further insights on the effect of ultrasound on the RuRu–ethanol activation, we have performed several additional experiments. Thus, first we have checked that nonsonicated ethanol solutions of **1** kept at 20 °C do not evolve with time (up to 50 days). To this end, we have prepared a solution of **1** and deposited on the substrate as described above for similar time periods. We have never found nano-organizations but trivial layer adsorption (Figure 5a). This result stresses the key role of sonication in the formation of one-dimensional structures. Second, since reorganization in the solid state of solvated species in chains has been previously reported,²⁴ we have tried to thermally activate the solvate species to obtain chains of compound **1** both on surface, after deposition of an ethanol solution of **1** and layer formation, and/or directly in solution. Thus we have performed a first experiment to investigate the possible thermal activation of these layers to

form one-dimensional structures without sonication. The experiments indicate that the flat surfaces observed upon by casting deposition of nonsonicated ethanol solutions of **1** on mica undergo significant changes, passing from a typical layer structure, with marked islands, to small clusters of about 12–14 nm height (Figure 5b). However, we have never observed formation of one-dimensional structures by simple heating. Finally, adsorptions on mica of droplets of heated (80 °C) nonsonicated ethanol solutions of **1** do not show any organization but again layer formation.

Now we proceed to study the effect of temperature in sonicated solutions. A solution of **1** in ethanol (3 g/L) was sonicated (for 2 h at 30 °C) and then diluted to 3×10^{-6} g/L and heated at 90 °C for 1 h (in a closed glass ampule). Afterward, a droplet (10 μL) of this solution was adsorbed on mica and studied by AFM. Figure 6a,b shows high density of micron-length fibers of **1** organized on bundles of variable heights. The formation of these organizations only requires 1 h in the hot solution after sonication. Therefore, we assume that a kinetic *versus* a thermodynamic control of the polymer formation has taken place in the sense that we do not obtain the equilibrium structure, but others which are in an equilibrium minimum that is not absolute. As expected, this experiment clearly shows that the temperature of the solution increases the speed of the bond formation between unsaturated species and, therefore, the polymer formation which in a shorter time reaches a large length. Moreover, when the former solution of **1** was stored for 2 h at 20 °C, and adsorbed on mica, the initial bundles evolved toward linear structures (Figure 6c). The typical heights of these straight fibers correspond to the expected diameter of a single molecule of **1**. This result is similar to that previously obtained in the above-described experiment (Figure 3) in which the sonicated solution of **1** was allowed to reach the thermodynamically stable situation after standing the solution at 20 °C for 43 days. The formation of fibers with a large persistence length can be rationalized by taking into account that the Ru–Ru–I

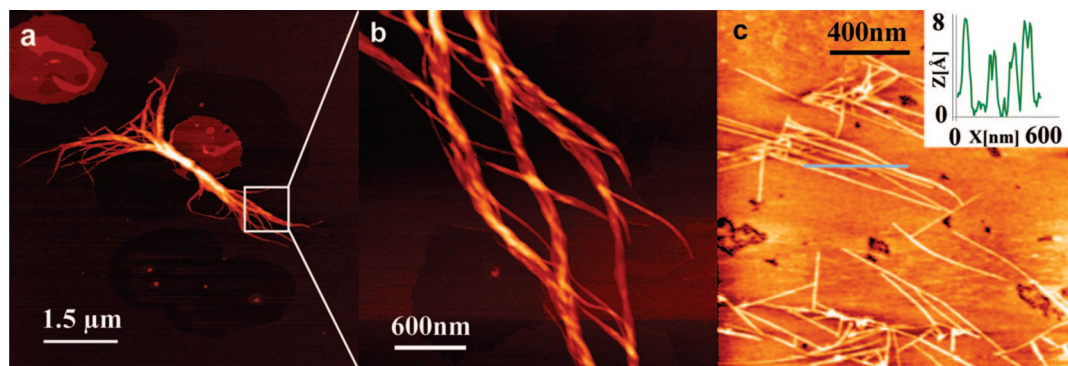


Figure 6. (a) AFM topographies of a sonicated ethanol solution of **1** after heating at 90 °C for 1 h, showing formation of large bundles. (b) A zoomed area of (a) with a height profile. (c) Evolution toward linear rods of the sonicated and heated solution (a) upon standing 2 h at 20 °C.

angle thermodynamically favors the value of 180°, as observed in the crystal structure.

In this work, we have demonstrated that the effect of the ultrasound is to induce scission of the coordination bonds giving rise to reactive species that self-organize in solution allowing a rich variety of structures. The recognition of these activated building blocks leads to isolation of very long individual chains of the MMX polymer when adsorbed on surfaces, as demonstrated by the AFM images. The ob-

served structures reproduce those present in the solution.

This work opens new paths to obtain low dimensional and well-organized entities of coordination polymers adsorbed on surfaces. Since some crystals of one-dimensional coordination polymers present remarkable electrical transport properties,^{4–6} the individual polymer chains can be potentially used as new molecular wires with rich chemical architectures. More classical molecular wires such as carbon nanotubes lack these properties.

EXPERIMENTAL METHODS

Solvents were obtained from commercial sources and used without further purification. Elemental analyses were carried out by the Microanalytical Service of the Complutense University of Madrid. IR spectra were recorded on a Shimadzu FT-IR Prestige-21 spectrophotometer using KBr disks. Molar conductivities were measured with a Philips PW 9526 digital conductivity meter using a Philips PW 9550/60 conductivity measuring cell. The variable-temperature magnetic susceptibilities were measured on polycrystalline samples with a Quantum Design MPMSXL SQUID (Superconducting Quantum Interference Device) susceptometer over a temperature range of 2 to 300 K at the constant field of 1 T. All data were corrected for the diamagnetic contribution of both the sample holder and the compound to the susceptibility. The molar diamagnetic corrections for the complexes were calculated based on Pascal's constants. Mass spectra were obtained on a Bruker Esquire-LC with electrospray ionization (ESI) using methanol as solvent. Nominal molecular masses and the isotopic distribution of all peaks were calculated with the MASAS computer program³³ using a polynomial expansion based on natural abundances of the isotopes.

Synthesis and Characterization of [Ru₂(μ-O₂CET)₄]_n (1**).** To a solution of [Ru₂Cl(μ-O₂CET)₄]_n (0.19 g, 0.35 mmol) in tetrahydrofuran (30 mL) was added AgBF₄ (0.068 g, 0.35 mmol). The mixture was stirred for 24 h in the dark giving a white precipitate of AgCl and a brown solution. The precipitate was filtered through Celite, and the solvent was removed under vacuum giving a brown solid. The solid, [Ru₂(μ-O₂CET)₄]BF₄, was dissolved in ethanol (10 mL) and treated with a saturated solution of KI in water (10 mL) giving a brown precipitate after 24 h, which was filtered, washed with water (3 × 20 mL), and dried under vacuum. Suitable single crystals for X-ray diffraction experiments of **1** were obtained by evaporation in air of a solution of this precipitate in methanol (40 mL). Yield 44%. Elemental analysis (%) calcd for **1**: C, 23.20; H, 3.24. Found: C, 23.22; H, 3.18. ESI-MS (MeOH): 496 [M + H – I]. IR (KBr): ν = 2981w, 2938w, 2879w, 1539w, 1466vs, 1426vs, 1369m, 1300s, 1244w, 1073m, 1008w, 891w, 808w, 666m, 425w cm⁻¹; μ_{eff} = 3.81 μ_B at room temperature.

X-Ray Data Collection and Structure Refinement. Data collection for compound **1** was carried out at room temperature on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The data were collected over a hemisphere of the reciprocal space by combination of three exposure sets, each exposure was of 20 s and covered 0.3° in ω. The first 100 frames were re-collected at the end of the data collection to monitor crystal decay, and no appreciable decay was observed. A summary of the fundamental crystal and refinement data is given in Table S1 in the Supporting Information.

The structures were solved by direct methods and refined by full-matrix least-squares procedures on F² (SHELXL-97).³⁴ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined riding on the respective carbon atoms. CCDC 683360 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12, Union

Road, Cambridge CB2 1EZ, UK [Fax: 0044-1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

AFM Studies. AFM images are acquired in dynamic mode using a Nanotec Electronica system. The images are processed using WSxM operating at room temperature in ambient air conditions.²⁷ **1** was deposited by solution casting: applying a drop of solution onto a freshly cleaved mica surface and allowing the solvent to evaporate. Olympus cantilevers were used with a nominal force constant of 0.75 N/m.

Preparation of the Substrates. In order to obtain reproducible results, Muscovite Mica (commercially available) was cleaved with adhesive tape just before deposition of solutions.

Sample Preparations. [Ru₂(μ-O₂CET)₄]_n (3 mg) in absolute ethanol (1 mL) was sonicated (680 W, 40 kHz) for 2 h at 30 °C. From this mother solution, diluted solutions of 3 × 10⁻⁶ g/L were prepared. Ten microliters of the eluted solution was deposited on a freshly exfoliated Muscovite mica substrate. The sample was left in air, allowing the complete evaporation of the solvent. To perform temperature studies, 0.2 mL of a 3 × 10⁻⁶ g/L solution of **1** in ethanol, prepared from the above mother solution, was heated in a closed glass ampule at 90 °C for 1 h. Then, 10 μL of this heated solution was deposited on a freshly exfoliated Muscovite mica substrate. The sample was left in air, allowing the complete evaporation of the solvent.

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Supporting Information Available: Temperature dependence of the molar susceptibility and magnetic moment, crystal data and structure refinement, bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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