# Supplementary Material (ESI) for Chemical Communications

# MMX polymer chains on surfaces

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# Experimental Procedures

## Synthesis and Characterization

**1**: To a solution of $Ru_2Cl(\mu\text{-}O_2CEt)_4$ (0.19 g, 0.35 mmol) in tetrahydrofuran (30 mL) $AgBF_4$ (0.068 g, 0.35mmol) was added. The mixture was stirred for 24 h in the dark giving a white precipitate of AgCl. This was filtered off over Celite and the solvent was removed under vacuum giving a brown solid. The solid obtained, $[Ru_2(\mu\text{-}O_2CEt)_4]BF_4$, was dissolved in ethanol (10 mL) and treated with a saturated solution of KBr in water (10 mL) giving a brown precipitate, which was filtered off, washed with water (3 x 20 ml) and dried under vacuum. Single crystals of **1** were obtained by evaporation in air of a solution of this precipitate in methanol. Yield 56 %. Elemental analysis (%) calcd for **1**: C 25.10, H 3.51; found: C: 24.84, H 3.42; IR (KBr): $\nu$ = 2983, 2941, 2879, 1468, 1427, 1370, 1302, 1246, 1076, 1010, 892, 809, 665 $cm^{-1}$; ESI-MS (MeOH): 496 $[M^{+}+H–Br]$.

Magnetic susceptibility was measured on a Quantum Design MPMSXL SQUID susceptometer and corrected for diamagnetic contributions.

The conductivity measurement in ethanol solution (39.81 $\Omega^{-1}.cm^{2}.mol^{-1}$) shows that this complex is an 1:1 electrolyte.[1] The corresponding value in water solution is 168.42 $\Omega^{-1}.cm^{2}.mol^{-1}$.

## Scanning Probe Microscopies

### Apparatus

Scanning Force Microscopy images were acquired in dynamic mode using a Nanotec Electronica system (www.nanotec.es). Olympus cantilevers were used with a nominal force constant of 0.75 N/m.

Scanning Tunnel Microscopy measurements were performed in ambient air conditions using a Nanotec Electronica system (www.nanotec.es).

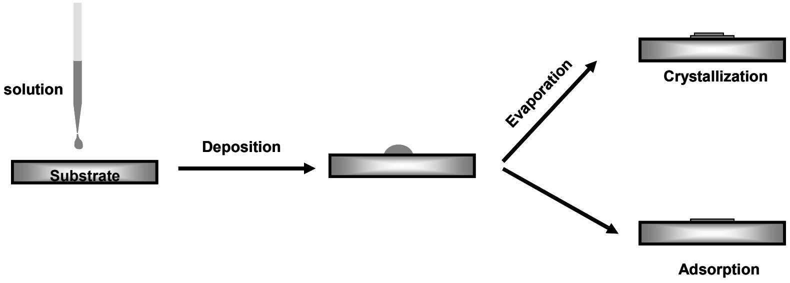
### Preparation of the Substrates

In order to obtain reproducible results, very flat substrates with precisely controlled chemical functionalities, freshly prepared just before the chemical deposition, were used. Two different commercially available supports were used: Muscovite Mica and Highly Oriented Pyrolitic Graphite (HOPG). Both of them were cleaved with adhesive tape.

## Sample Preparations for AFM

*Procedure (a).* [$Ru_2Br(\mu\text{-}O_2CEt)_4$]$_n$ (0.5 mg) in absolute ethanol (1 mL) was sonicated (680 W, 40 kHz) for 15 min. at 20 ºC and the clear solution filtered off. From this mother solution, diluted solutions of $10^{-8}$ g/L were prepared. A volume of 50 μL was deposited on a freshly exfoliated mica sheet. The sample was left in air allowing the complete evaporation.

*Procedure (b).* [$Ru_2Br(\mu\text{-}O_2CEt)_4$]$_n$ (5 mg) was suspended in 1 mL of a water-sodium dodecyl sulfate (0.1 % w.) solution and sonicated (410 W, 40 kHz) for 90 min. at 20 ºC. The suspension was centrifuged (9000 rpm) for 20 min. and 50 μL of the clear solution was deposited on a freshly exfoliated mica sheet. Then, the sample was left in air for 10 min. avoiding the dryness. Finally, the mica surface was rinsed gently with water and dried under nitrogen.



*Scheme S1:* Casting deposition of the [$Ru_2Br(\mu\text{-}O_2CEt)_4$]$_n$ on the substrate.

## Sample Preparation for STM

$[Ru_2Br(\mu\text{-}O_2CEt)_4]_n$ (1 mg) in absolute ethanol (1 mL) was sonicated (680 wat. 40 kHz) for 70 min. at 20 ºC. The solution was then diluted up to $10^{-10}$ g/L and 20 µl of this solution were deposited on HOPG substrate. After solvent evaporation imaging was performed, the tunnel currents were varied between 0.1 and 0.5 nA and a bias voltage closed to 100 mV. Atomic periodicity resolution was obtained in zones without molecules (and in some cases in the vicinity of the molecules). Mechanically cut Pt/Ir tips were used in all the experiments.

## Comments to the STM experiments

HOPG is a flat surface that, however, exhibits a large number of defects when imaged with STM. Some of these defects produce structures that may resemble DNA. These type of structures were described in the early times of STM.[2,3] However, to image them was not an easy task. In the STM experiments carried out with compound **1**, we found structures represented in Fig 3 very often with AFM, only after molecule deposition (not in HOPG blanks) and it was indeed the case with STM. If the molecules were not previously deposited we may certainly find similar one-dimensional structures to those reported by Clemmer and Beebe[2] but with a relatively low frequency. Besides, while we also observed the Moiré lattices and other defects usually presented on HOPG, we have never observed any so open and clear one-dimensional spiral structure on blank graphite with STM.

## References

1. W.J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81
2. C. R. Clemmer, T. P. Beebe, *Science*, 1991, **251**, 640.
3. W.T. Pong, C. Durkan, *J. Phys. D: Appl. Phys.*, 2005, **38**, 329.

**Figure S1.** Temperature dependence of the molar susceptibility $\chi_M$(circles) and $\mu_{eff.}$ (triangles) for **1**; solid lines are the product of a least-square fit to the model indicated in the text.

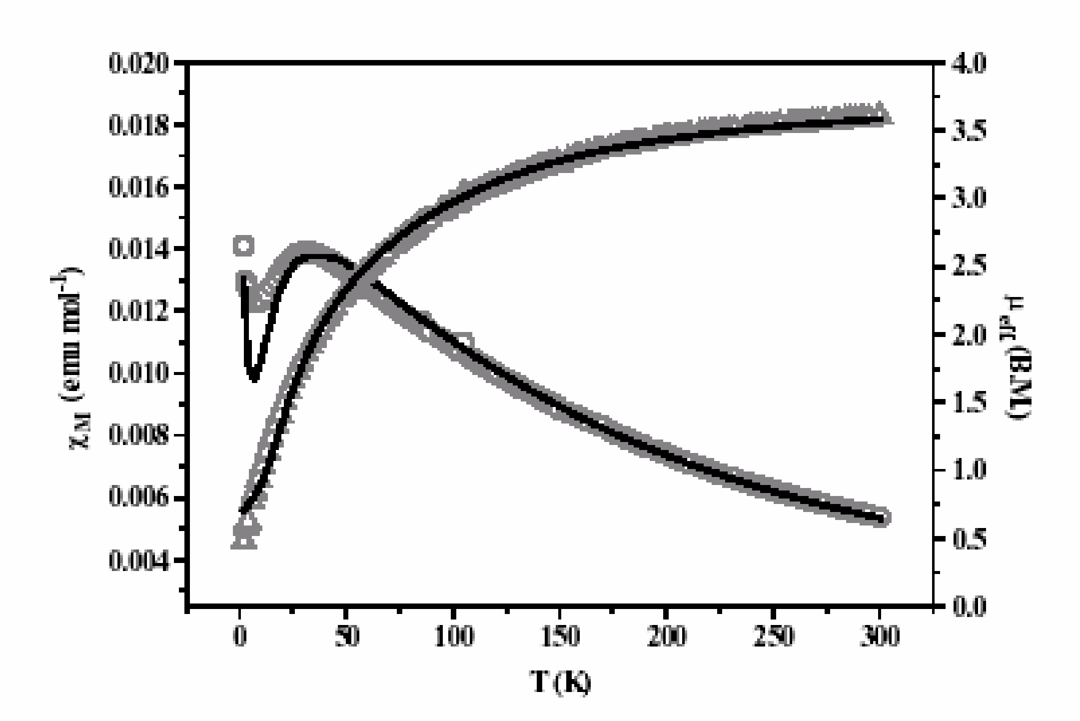


**Figure S2.** STM topographic image of a fibre. The atomic periodicity allows observing that the fibres follow the general direction of graphite atoms (arrows).