Intrinsic electrical conductivity of nanostructured metal-organic polymer chains

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One-dimensional materials have given rise to great expectations because of their potential utility in the emerging technology of flexible and transparent electronics^[1]. Molecular materials have shown promising electronics properties at the macroscale but just recently it has been demonstrated that they can be assembled to nanostructures exhibiting outstanding conductivity^[2]. However, despite years of research on the macro- and nano-scale, structural disorder represents the major hurdle in achieving high conductivities^[2,3]. Moreover, a good understanding that relates the properties observed at the nano and macro scale is still missing.

Here we focus on the electronic transport properties of nano and macrostructures of a coordination polymer $[Pt_2(dta)_4l]_n$ (*dta*= dithioacetate) named as MMX ^[4]. We report ^[5] measurements of highly ordered metal-organic nanoribbons, with inherent metallic character, whose intrinsic (defect free) conductivity is found to be 10^4 Sm⁻¹, three orders of magnitude higher than that of our macroscopic crystals. This magnitude is preserved for distances as large as 300 nm. Above this length, the presence of structural defects gives rise to an inter-fibre-mediated charge transport similar to that of macroscopic crystals.

The well-ordered 1D nanostructures have been isolated on SiO_2/Si substrate by direct sublimation from monocrystals of $[Pt_2(dta)_4I]_n$ under high vacuum conditions. The electrical transport properties of the nanomaterials were characterized by Conductive Atomic Force Microscopy (C-AFM) at room temperature ^[6]. The first direct experimental evidence of the gapless electronic structured predicted ^[7] is also found by Field Effect Transistor configuration measurements.

In summary, to overcoming low conductivities and to clarify the charge transport mechanisms at the nano and macroscale (and their contributions), disorder should be reduced until the studied sizes are in a range where it can be ignored. To reverse this situation, we have simultaneously achieved a high structural order and electrical characterization at the nanometre scale, as well as at the macroscale, allowing us to make a comprehensive approach about the electrical properties that govern this MMX polymer. This was possible due to the excellent processability of these metal organic polymers^[8], which show the exceptional feature of undergoing reversible depolymerization/repolymerization during sublimation.

This work constitutes a unique case of study of the influence of a small concentration of defects in metal-organic systems with high electrical anisotropy and the ideas and methodology presented here are expandable to other similar polymeric compounds and can be applied to the study of the emerging nanostructured metal-organic polymer family.

Finally, the experimental results postulate metal-organic molecular wires as good metallic interconnectors in nanodevices.

References

[1] Ju, S. Y. et al., Nature Nanotechnology, 2 (2007) 378.

- [2] Welte, L. et al., Nature Nanotechnology, 5 (2010) 110.
- [3] Tuccitto, N.. et al., Nature Materials, 8 (2009) 41.
- [4] a) Bellito, C. Et al., *Inorganic Chemistry*, **22** (1983) 449. ; b) Kitagawa, H. *et al.*, *Journal of the American Chemical Society*, **121** (1999) 10068.
- [5] Hermosa, C. et al., *Nature Communications*, **4** (2013) 1.
- [6] de Pablo, P. J. et al., *Physical Review Letters*, **3** (2002) 36804.
- [7] Calzolari, A. et al., Journal of the American Chemical Society, 130 (2008) 5552.
- [8] Welte, L. et al., Advanced Materials, 20 (2009) 2025.



Figure 1. Growth of nanoribbons with high degree of order by crystal sublimation (a) Structure of a $[Pt_2(dta)_4l]n$ (dta= dithioacetato) single fibre. (b,c) AFM images of nanoribbons on a SiO₂ substrate where the straightness and height homogeneity can be appreciated. The inset in c is a profile acquired on the green line of the corresponding image, where the cross-section of the ribbons can be determined (Typical dimensions of the nanoribbons are 10 μ m_100 nm_20 nm).



Figure 2. Electrical characterizations by conductive AFM of **(a)** MMX nanoribbons and **(b)** MMX crystals. The plots display Resistance versus length curves in a semi log (a) and in a linear scale (b). **(c)** Experimental I/V curves obtained for nanoribbons (green), and crystals both for longitudinal transport (blue) and for transversal transport (red).