Intrinsic electrical conductivity of nanostructured metal-organic polymer chains

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One-dimensional conductive polymers are attractive materials because of their potential in flexible and transparent electronics. Despite years of research, on the macro- and nano-scale, structural disorder represents the major hurdle in achieving high conductivities. Here we report measurements of highly ordered metal-organic nanoribbons, whose intrinsic (defect-free) conductivity is found to be $10^4$ S m$^{-1}$, 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 (~ 0.5%) gives rise to an inter-fibre-mediated charge transport similar to that of macroscopic crystals. We provide the first direct experimental evidence of the gapless electronic structure predicted for these compounds. Our results postulate metal-organic molecular wires as good metallic interconnectors in nanodevices.
Among other nanostructures, one-dimensional (1D) materials have given rise to great expectations because of their unique electrical transport properties as well as their potential utility in the emerging technology of transparent and flexible electronics. For more than three decades, conjugated organic polymers were positioned as the best candidates for these purposes and they were extensively studied both at macro- and nano-scale. Although remarkable improvement in their processability was achieved, the charge transport mechanisms and the limited conductivity found in fibres of organic polymers are still a matter of discussion. They show features typical of disordered materials where charge transport is described in terms of metallic islands surrounded by disordered regions that act as barriers. In the 1990s, this issue seemed to be resolved with the appearance of carbon nanotubes, purely carbon-based crystalline cylinders that exhibited unprecedented high conductivities. Although the first reports showed promising results, considerable effort was required to understand the tremendous influence of atomic scale defects on their conductivity. Up to now, the lack of a cheap and massive procedure for the production of tubes with controlled chirality and low defect content has hindered their applicability. More recently, nanostructures based on metal-organic compounds have been proposed as a viable and promising alternative. These compounds allow the rational design of materials by self-assembly of selected building blocks. However, the conductivities reported so far for nanostructures and layered materials of metal-organic compounds are limited, as in organic polymers, by structural disorder. Therefore, the challenge of overcoming low conductivities and clarifying charge transport mechanisms relies on the production of well-ordered nanostructures and the ability to access their electrical properties below the length where disorder has a relevant role. In this work, we report the production of highly ordered nanoribbons where we are able to simultaneously achieve these two milestones.

To this aim, we focus on the 1D MMX metal-organic polymer [Pt2(dta)I]n, formed by two simple moieties: a dimetallic subunit with two platinum centres connected by four bridging acetate ligands and an iodine atom bridging the dimetallic units. By direct sublimation of monocrystals of [Pt2(dta)I]n on SiO2/Si supports, we form nanoribbons with a high degree of structural perfection. Each nanoribbon is composed of thousands of parallel MMX chains of ~0.8 nm diameter interacting by weak Van der Waals forces. While the interatomic electron density along the chain is predicted to be high, in the transversal direction, the electron density between chains is almost zero. This anisotropy gives rise to an extreme difference between the longitudinal (along the nanoribbon axis) and transversal electrical conductivities. The nanoribbons prepared in this way are characterized by conductive atomic force microscopy (CAFM). The small contact area characteristic of CAFM, along with the high electrical anisotropy of the material, reduces the paths of the current from thousands of chains to ~10. Plots of resistance versus length allow the intrinsic conductivity as well as the distance between defects, which dramatically influence charge transport, to be estimated. These are found to be 10^4 S m^-1 and ~200 nm, respectively. Direct evidence of their inherent metallic character is also found, in good agreement with theoretical predictions. When the electrical conduction properties of the nanoribbons are compared with those of the original crystals sublimated to prepare the nanoribbons (with dimensions in the range of 10–300 μm), we obtain a significant improvement of three to four orders of magnitude. Interestingly, the electrical resistance of the conventional crystals scales linearly with the length of the crystal, in contrast with the exponential dependence observed for nanoribbons. The relationship between nano- and macro-scale properties is rationalized in terms of effective medium theory, showing that the inter-fibre transport is the limiting process in the crystals while transport along the polymeric chains dominates in the nanoribbons.

**Results**

**Electrical transport in nanoribbons.** Figure 1a provides a schematic representation of a single chain of [Pt2(dta)I]n. The crystals were synthesized and characterized as described in Bellitto et al. The nanoribbons were prepared by sublimating these crystals under high vacuum conditions on SiO2(300 nm)/Si(100) substrates previously treated with oxygen plasma (details can be found in the Methods section and Supplementary Figs S1 and S2). AFM images of the resulting nanoribbons are shown in (b, c, d). The small contact area characteristic of CAFM, along with the high electrical anisotropy of the material, reduces the paths of the current from thousands of chains to ~10. Plots of resistance versus length allow the intrinsic conductivity as well as the distance between defects, which dramatically influence charge transport, to be estimated. These are found to be 10^4 S m^-1 and ~200 nm, respectively. Direct evidence of their inherent metallic character is also found, in good agreement with theoretical predictions. When the electrical conduction properties of the nanoribbons are compared with those of the original crystals sublimated to prepare the nanoribbons (with dimensions in the range of 10–300 μm), we obtain a significant improvement of three to four orders of magnitude. Interestingly, the electrical resistance of the conventional crystals scales linearly with the length of the crystal, in contrast with the exponential dependence observed for nanoribbons. The relationship between nano- and macro-scale properties is rationalized in terms of effective medium theory, showing that the inter-fibre transport is the limiting process in the crystals while transport along the polymeric chains dominates in the nanoribbons.

**Figure 1** | Growth of nanoribbons with high degree of structural perfection by crystal sublimation. (a) Structure of a [Pt2(dta)I]n (dta = dithioacetato) single fibre. (b,c,d) AFM images of nanoribbons on a SiO2 substrate where the straightness and height homogeneity can be appreciated. The inset in (d) 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 μm x 100 nm x 20 nm. Scale bars, 8, 4 and 0.1 μm (for b, c and d, respectively).
in Fig. 1b–d. Subsequent to nanoribbon growth, a macroscopic electrode was deposited by thermal evaporation of gold using a convenient stencil mask. The final result is a long gold electrode edge that partially covers a number of nanoribbons. The electrical resistance of the nanostructure was probed by CAFM25,26. Figure 2a shows a representative AFM image of a nanoribbon protruding from a gold electrode, and a scheme of the electrical circuit was used to characterize the ribbon. Figure 2c displays the electrical resistance $R$, as a function of the distance between electrodes $L$, obtained for a representative nanoribbon. The resistance displays an initial region where it barely depends on length followed by a rapid increase that can be fitted well to an exponential law. The current versus voltage ($I/V$) curves acquired for the nanoribbons and depicted in Fig. 2b show a linear dependence, and hence the resistance for each data point in Fig. 2c is independent of the bias voltage.

The observed non-linear dependence of $R(L)$ suggests that electron–defect interactions are the main source of resistance in these nanoribbons and can be explained with a simple model of polymeric chains connected in parallel. We assume that these nanoribbons and can be explained with a simple model of electron–defect interactions are the main source of resistance in the data shown in Fig. 2c leads to $R_{1D} \approx 0.1 \text{M} \Omega \text{nm}^{-1}$, $A \approx 212 \text{nm}$ and $R_e \approx 2 \text{M} \Omega$. The exact values change for different nanoribbons, but the ranges are small ($0.02 < R_{1D} < 0.1$, $124 < A < 230 \text{nm}$ and $1 < R_e < 2 \text{M} \Omega$). The estimated density of defects $c$ is $0.4–1\%$ (see Supplementary Note 2 for details), implying that there is one defect every $80–210 \text{nm}$ in each polymeric chain. Ideally, if we could prepare defect-free crystals, their intrinsic three-dimensional (3D) conductivity would be $\sigma_{3D} \approx 2 \times 10^4 \text{S m}^{-1}$, higher than that reported for the best conjugated polymer nanofibres.10 In the present nanoribbons, this intrinsic conductivity occurs for lengths as large as a few hundred nanometres.

The $I/V$ curves (Fig. 2b) show a clear linear dependence independently of the position at which the curve is measured, suggesting an inherent metallic character. Although this metallic behaviour has been predicted by density functional theory calculations16,24, it has not yet been observed experimentally. To corroborate this behaviour, we performed electrical transport measurements in a field effect transistor configuration (see Methods section and Supplementary Figs S3 and S4). The absence of gate-dependent resistance confirms the gapless band structure. The results were similar for both high (Au) and low (Ti) work function metals, ruling out injection or contact effects.

Because we perform superficial contacts, we consider that only the wires directly contacted by the AFM probe contribute to the electrical current. Because of the high electrical anisotropy of the nanoribbons, those in the second layer or outside the tip contact area will exhibit a much higher electrical resistance and can be safely neglected. The number of wires contacted by the AFM tip can be estimated using Hertz’s model, as explained in Welte et al.16 and in the Supplementary Note 1. The contact region has a circular shape with a typical diameter of $\sim 12 \text{nm}$. As the distance between chains is $\sim 0.8 \text{nm}$, according to X-ray data23, $N_0 \sim 10–20$. For all the measured nanoribbons, the experimental $R(L)$ curves are fitted well by equation (1). Numerical fitting of the data shown in Fig. 2c leads to $R_{1D} \approx 0.1 \text{M} \Omega \text{nm}^{-1}$, $A \approx 212 \text{nm}$ and $R_e \approx 2 \text{M} \Omega$. The exact values change for different nanoribbons, but the ranges are small ($0.02 < R_{1D} < 0.1$, $124 < A < 230 \text{nm}$ and $1 < R_e < 2 \text{M} \Omega$). The estimated density of defects $c$ is $0.4–1\%$ (see Supplementary Note 2 for details), implying that there is one defect every $80–210 \text{nm}$ in each polymeric chain. Ideally, if we could prepare defect-free crystals, their intrinsic three-dimensional (3D) conductivity would be $\sigma_{3D} \approx 2 \times 10^4 \text{S m}^{-1}$, higher than that reported for the best conjugated polymer nanofibres10. In the present nanoribbons, this intrinsic conductivity occurs for lengths as large as a few hundred nanometres.

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**Figure 2 | Electrical characterisation of MMX nanoribbons by conductive AFM.** (a) Scheme of the electronic circuit used to measure the current flowing through the nanoribbons, a metallized AFM tip is used as a mobile electrode. (b) $I/V$ curves obtained at different distances between electrodes (lengths) for the same nanoribbon. Here it can be clearly seen that the linear behaviour is maintained for every point. Resistance is calculated as the inverse of the slope of these graphs. (c) Resistance versus length, in a linear scale, for the same nanoribbons as data depicted in b. The inset displays a semi log plot of the same experimental data. Black dots represent experimental measurements and grey line is a fit to $R = R_e + R_{1D} \frac{L}{N_0} \exp(L/A)$. 

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The inset shows an optical microscopy image of a crystal contacted by two gold probes. (C0/)

measurements (perpendicular to the polymer chains axis) resulted in values of $10^{-4}$–$10^{-3}\, \text{S}\, \text{m}^{-1}$, three or four orders of magnitude lower than those obtained for the intrinsic value of the polymeric chains. In contrast with the exponential $R(L)$ dependence of the nanoribbons, the electrical resistance of the crystal as a function of the length (Fig. 3a) showed a linear dependence. In addition, the curves showed a marked non-linear behaviour (Fig. 3b), clearly indicating a change in the electrical transport mechanism from the nanoribbons to the crystals. Two-terminal transversal conductivity measurements (perpendicular to the polymer chains axis) resulted in values of $10^{-4}$–$10^{-3}\, \text{S}\, \text{m}^{-1}$, reflecting the very high electrical anisotropy in the electrical properties of these crystals.

**Electrical transport in conventional crystals.** With the aim of a full characterization of the material, the measurements were extended to conventional (micro-scaled) monocrystals of the same compound with typical dimensions of $350 \times 10 \times 10\, \mu\text{m}^3$. Measurements of several crystals, in four-probe configuration, gave longitudinal conductivity values of $10–80\, \text{S}\, \text{m}^{-1}$, three or four orders of magnitude lower than those obtained for the intrinsic value of the polymeric chains. In contrast with the exponential $R(L)$ dependence of the nanoribbons, the electrical resistance of the crystal as a function of the length (Fig. 3a) showed a linear dependence. In addition, the curves showed a marked non-linear behaviour (Fig. 3b), clearly indicating a change in the electrical transport mechanism from the nanoribbons to the crystals. Two-terminal transversal conductivity measurements (perpendicular to the polymer chains axis) resulted in values of $10^{-4}$–$10^{-3}\, \text{S}\, \text{m}^{-1}$, reflecting the very high electrical anisotropy in the electrical properties of these crystals.

**Numerical simulations.** In crystals with lengths $L \gg A$, all polymeric chains have at least one defect and, hence, transport perpendicular to the polymer chains becomes determinant. This regime dominates for microscopic samples. To study the transition between the $L \leq A$ and $L \gg A$ regimes, we performed extensive numerical simulations in an anisotropic 3D resistor model (Supplementary Note 2 for details). These simulations support the $R(L)$ dependences observed in both the nanoribbons and the crystals (Fig. 4) and confirm that the regime observed in crystals can be understood using the Effective Medium Theory applied to anisotropic systems (Supplementary Note 3)\textsuperscript{28–30}. This theory relates effective conductivities, $\sigma_{\parallel\text{eff}}$ and $\sigma_{\perp\text{eff}}$, measured in macroscopic crystals, and intrinsic (free of defects) conductivities, $\sigma_{\parallel\text{int}}$ and $\sigma_{\perp\text{int}}$, measured using CAFM, where $\parallel$ and $\perp$ indicate the directions parallel and perpendicular to the polymeric chains, respectively. Considering that the only source of disorder is the chain-interrupting defect, we assume that $\sigma_{\perp\text{eff}} = \sigma_{\perp\text{int}}$. With such a limit, high anisotropy and small defect concentration, the effective conductivity decreases to the simple expression $\sigma_{\parallel\text{eff}} = \sigma_{\perp\text{eff}} \times 0.918/c^2$ independently of the sample size, as found experimentally. From this expression, we calculate that the defect densities for both crystals and nanoribbons are very similar (0.4% $< c < 1\%$), see Supplementary Fig. S5. The simulations also disclose a crossover regime ($L \approx A$), which matches the nanoscopic and microscopic regimes. Details about this crossover regime and a simple analytical fit to the numerical data are given in the Supplementary Note 4 and Supplementary Figs S6 and S7.

**Discussion**

The situation in which the charge transport mechanism at the nanoscale is completely different to the processes dominating charge transport at the macroscale has been previously observed in conjugated conducting polymers\textsuperscript{31}. To clarify these mechanisms and their contributions, disorder should be reduced until the studied sizes are in a range where it can be ignored. For the case of organic polymers, this situation has been historically too difficult to reach, and charge transport mechanisms are still a matter of intense debate. The situation for metal-organic materials was analogous until now. To reverse
this situation, we had to simultaneously achieve a high structural order and characterization at the nanometre scale. This was possible due to the excellent processability of these metal-organic polymers, which show the exceptional feature of undergoing reversible depolymerization/repolymerization during sublimation, as well as the fine tuning of the parameters affecting the repolymerization process on the surface. Although the achieved characteristic length of 200 nm is already enough for many current devices, our on-going work focuses on increasing this distance further.

Finally, in the case of quasi-1D systems, it is known that electron–electron interactions lead to phases that are different from conventional Fermi liquids, such as Luttinger Liquids or Wigner Crystals. Some experimental studies on polymer nanofibres and nanotubes have already shown features characteristic of 1D systems. In our crystals, while fits to conventional hopping models show a poor agreement, the I(V) curves in the parallel direction can be fitted by

\[ I = \frac{G(V)}{V/K_{B}T} \left( 1 + 0.5a \frac{V}{2k_{B}T} \right)^{2} \]  

Where \( I \) is the Gamma function, \( V \) is the bias voltage, \( T \) is the temperature (300 K) and \( K_{B} \) is the Boltzmann constant, suggesting a 1D electronic behaviour with a single band crossing the Fermi level. The fitting values are \( I_{0} = 0.12 \text{nA}, \beta = 0.937 \) (the critical exponent for the density of states) and \( G_{N} = 0.185 \times 10^{-7} \text{S} \), which represents a parallel conductance. Unfortunately, temperature-dependent measurements in these samples are challenging and difficult to interpret due to a crystal structural transition near room temperature. A complete identification of such 1D behaviour would require temperature-dependent studies on nanoribbons, and work in this respect is currently underway.

In summary, we demonstrate that highly ordered platinum-based MMX 1D structures are able to transport electrical carriers more efficiently than 1D conjugated organic polymers. By taking advantage of the self-assembly capability of this compound, we have been able to prepare, in an easy way, 1D structures, with low defect content (0.4% < c < 1%), that present an intrinsic conductivity of 10\(^{4} \text{ S m}^{-1}\). Also, owing to the low structural disorder, we have been able to experimentally confirm the predicted gapless band structure of this material. 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. The ideas and methodology presented here are expandable to other similar polymeric compounds and can be applied to the study of the emerging nanostructured met-organic polymer family.

**Methods**

**Crystal sublimation and structural characterization of ribbons.** Well-ordered 1D nanoribbons on SiO\(_{2}\) surfaces were isolated by direct sublimation from organic polymers, which show the exceptional feature of being expandable to other similar polymeric compounds and can be used. AFM inspection of the substrate revealed nanoribbons that contacted both fixed electrodes, and the distance between the electrodes was 0.4 and 1.5 µm. The variation of the current versus bias applied across the nanoribbons as a function of the back-gate voltage was measured (Supplementary Fig. S4). Measurements were performed both in an ambient and an argon atmosphere. No difference was detected.

**Electrical characterisation of the nanoribbons in a field-effect configuration.** Samples for electrical characterisation in FET configuration were prepared by metal vapour deposition with a stencil mask on SiO\(_{2}\)/Si/metal substrates with previously deposited nanoribbons (Supplementary Fig. S3). Gold and titanium electrodes were used. AFM inspection of the substrate revealed nanoribbons that contacted both fixed electrodes, and the distance between the electrodes was 0.4 and 1.5 µm. The variation of the current versus bias applied across the nanoribbons as a function of the back-gate voltage was measured (Supplementary Fig. S4). Measurements were performed both in an ambient and an argon atmosphere. No difference was detected.

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**Author contributions**

C.H. and C.G.-N. conducted the experiments. M.-R.A. synthesized the MMX crystals. J.V.A., M.F. and J.M.S. planned and performed the models and calculations, designed the theoretical work and prepared the manuscript. C.G.-N., J.G.-H. and F.Z. designed the experiments, analysed the data and prepared the manuscript. All authors participated in discussion.

**Additional information**

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