Electron-beam induced formation of nanoparticle chains and wires from a ruthenium cluster polymer

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The novel organometallic cluster polymer of probable formula $[Ru_6C(CO)_{15}Ph_2PC_2PPh_2]_n$ ($n = ca.$ 1000) 1 has been prepared and, on irradiation in an electron beam, forms first nanoparticle chains and then conducting wires.

The potential of simple organic and inorganic molecules as precursors in the formation of electronic devices by direct chemical synthesis is substantial. Well-studied examples include carbon nanotubes,[1] novel resists,[2] metal[3] and semiconducting colloids[4] and conducting and semiconducting polymers.[5] A wealth of physical phenomena have been observed for these examples varying from zero-dimensional electronic confinement[6] to a wide variety of field-effect transition (FET) structures.[7]

Here we report a further type of compound which offers considerable potential in its application to new electronic devices. Until recently, carbonyl clusters have received little attention in this connection, partly because of their relatively small size, and partly because of the difficulty in performing standard microelectronic fabrication. We now report that these difficulties may be largely overcome by the use of materials containing clusters bonded *within* a polymer backbone.

A number of organometallic polymers have been reported previously. These range from those with pendant organometallic fragments attached to polymeric organic backbones[8] to those with metallic species incorporated into the backbone.[9] A common method of incorporation of a metal as a pendant is by performing a polymerisation on a functionalised unit, *e.g.* the free radical polymerisation of vinylferrocene.[10] Other polymers in this class include rigid-rod transition metal–acetylide polymers which usually involve group 10 metals or gold; these polymers consist of metals linked by organic spacers with a minimum capacity to bend. This is achieved by using alkyne or aromatic groups alternately to form rigid rods. In these systems

the metal has been shown to coordinate in a *trans* fashion.[11] The electrical and electrochemical properties of such materials have not been investigated in detail.

Here, we report: (i) the synthesis and characterisation of the first organometallic polymer with carbonyl clusters in the backbone formulated as $[Ru_6C(CO)_{15}Ph_2PC_2PPh_2]_n$ and (ii) the processing of this material by electron beam exposure into nanowires with tunable conduction characteristics.

The new cluster based polymer $[Ru_6C(CO)_{15}(Ph_2PC_2PPh_2)]_n$ was synthesised from the direct reaction of $[Ru_6C(CO)_{17}]$ with the alkyne linking reagent $[Ph_2PC_2PPh_2]$ in tetrahydrofuran under reflux. After 5 h, removal of the solvent, followed by precipitation from dichloromethane, hexane gives the polymeric derivative $[Ru_6C(CO)_{15}Ph_2PC_2PPh_2]_n$ 1 as a dark brown powder which is soluble in dichloromethane.† Other products 2–4 may also be separated from other reaction stoichiometries. These have been identified as $[Ru_6C(CO)_{16}PPh_2C_2PPh_2]$ 2, $Ru_6C(CO)_{15}\{PPh_2C_2PPh_2\}_2$ 3 and $[Ru_5C(CO)_{13}PPh_2C_2PPh_2]$ 4.† Significantly, in a separate experiment, we have observed that compound 3 undergoes reaction with a stoichiometric amount of $[Ru_6C(CO)_{17}]$ to yield polymer 1. We believe that the polymer consists of $[Ru_6C(CO)_{15}]$ units linked by $[Ph_2PCCPPh_2]$ ligands (Fig. 1). The polymer 1 has been identified by routine chemical analysis. Elemental analyses (C, H) are totally in accord with the proposed empirical formula, and the presence of phosphorus is further confirmed by the solid state ^{31}P NMR† which exhibits a broad band at $\delta -20$. In the IR spectrum a broad $\nu(CO)$ band is observed† consistent with a polymer containing a large number of bonded CO ligands. A molecular weight of 1000–1020 has been estimated from electon microscopy carried out on several samples. This technique has been developed from our TEM studies of other systems.[12] In brief, a monolayer of polymer was deposited from solution onto holey carbon microscopy grids. The images over
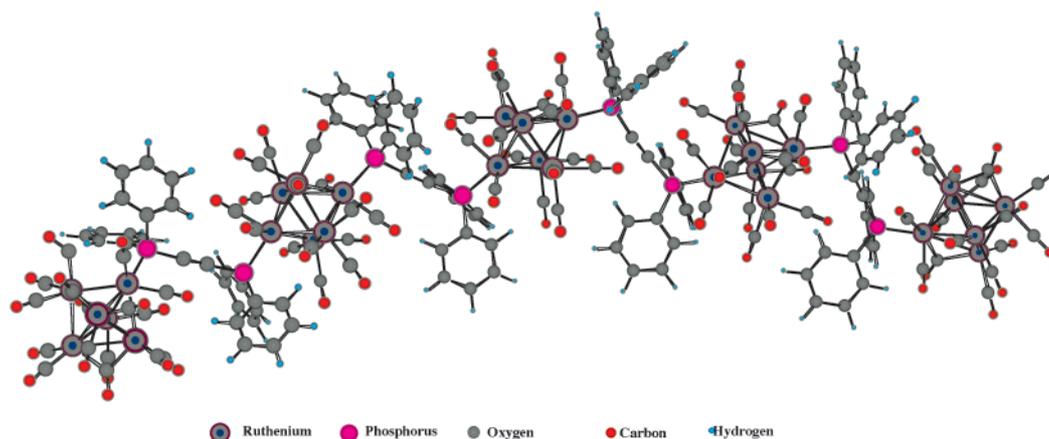

Ruthenium ● Phosphorus ● Oxygen ● Carbon ● Hydrogen

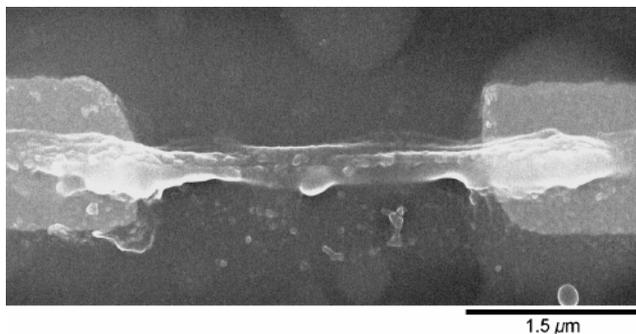**Fig. 1** The proposed structure of $[Ru_6C(CO)_{15}(Ph_2PC_2PPh_2)]_n$.

Fig. 2 SEM micrograph of a typical device. The polymeric nanowire (300 nm in width) lies on top of the gold contacts.

time showed that the polymer was very beam sensitive but from the initial images of chains of clusters an estimate of chain length could be determined. Further studies were made on the polymer supported on silica spheres (*ca.* 5 nm in diameter) to confirm and follow the nanoparticle growth induced by the electron beam (*vide infra*). This work will also be dealt with in a more detailed manner in a full paper.

Silicon substrates coated with 200 nm of high-quality oxide were prepared with micro-fabricated contacts composed of 10 nm Cr and 30 nm of Au (Fig. 2). The contacts defined a region for investigation of 4×5 μm, orientated with the shorter direction along the current path. A freshly prepared solution of polymer **1** in dichloromethane (200 mg ml^{-1}) was filtered through Teflon (200 nm pore size) and then spin-coated onto the substrate forming a layer *ca.* 120 nm thick. The layers were smooth and uniform and largely free from visible imperfections. Following preparation, exposures were performed on the samples in the usual way by electron-beam lithography (accelerating voltage 60 kV, current 1 nA, beam diameter *ca.* 250 nm). Exposures were conducted at 25 °C in a vacuum of 10^{-4} Pa or better. After development for 1 min, the polymeric material was observed to behave as a negative electron beam resist, with a sensitivity of 400 C m^{-2}. Atomic force microscopy (AFM) was used to determine the thickness of the material after development. At this stage the conductivity of the material was found to be immeasurably small. However, after more extensive electron beam exposures (accelerating voltage 60 kV, current 10 nA, beam diameter 1 μm at doses ranging from 10^3 to 4×10^6 C m^{-2}) the films showed conductivity increasing in a power law as a function of dose. The conduction mechanism was found to be variable range hopping in two dimensions[13] (Fig. 3). Using a finely focussed electron beam, it was possible to make wires as small as 100 nm in width. A typical device is shown in Fig. 2. The current–voltage characteristics near room temperature are well fitted by a hyperbolic sine, as predicted by variable-range hopping theory. However, at low temperatures, the current is strongly suppressed at low bias voltage.

We postulate that in the initially formed polymer the cluster units are surrounded by the non-conducting carbonyl sheath but that on initial irradiation with the electron-beam this sheath is lost to produce nanoparticle chains thus accounting for the observed contraction in volume. Weight loss as measured by tga tends to support this view. Further irradiation is then considered to bring about the fusion of groups of these particles into larger clusters, forming a conducting chain. We consider that this conductivity is brought about by an electron hopping process between nanoparticle groups rather than through the formation of a continuous metal wire. At low temperature, the device characteristics observed are consistent with charging-suppressed transport through these groups.
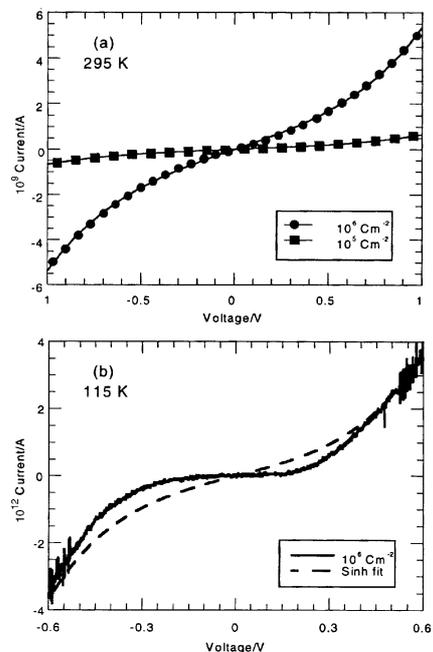
Fig. 3 Conductance/dose characteristics for two nanowires. All fits are hyperbolic sine functions.

Notes and references

† Compound **1** identified as [Ru$_6$C(CO)$_{15}$Ph$_2$PC$_2$PPh$_2$]$_n$ [FTIR: υ(CO) 2009br cm^{-1} br; **2** identified as [Ru$_6$C(CO)$_{16}$PPh$_2$CCPPh$_2$)] [*m/z* 1492.26 (M + MeO$^-$); FTIR: υ(CO) 2084.6w cm^{-1}, 2032.8s cm^{-1}]; **3** identified as Ru$_6$C(CO)$_{15}$[PPh$_2$CCPPh$_2$]$_2$ [*m/z* 1859.43 (M + MeO$^-$); δ$_P$(H$_3$PO$_4$ −30.4(s), 12.3 (s); FTIR: υ(CO) 2065.9m, 2018.4vs, 1970.2 (sh) cm^{-1}]; **4** identified as Ru$_5$C(CO)$_{13}$PPh$_2$CCPPh$_2$ by X-Ray crystal analysis. [*m/z* 1306.9 (M + MeO$^-$); FTIR: υ(CO) 2075.3w, 2053 s, 2016.5 cm^{-1} s, 1991.7 (sh) cm^{-1}; solid state MAS NMR: δ$_P$ −20 (s, br) with side bands at δ −80 and +40; δ$_C$ 125 (qnt, br)]

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