Nanostructures on surfaces of the metalorganic compound $\{Fe_2(CO)_6[\mu\text{-}S_2C_6H_2(OH)_2]\}$ and its potential as catalyst precursor for the synthesis of carbon nanotubes

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Supporting Information

Experimental Procedure

Materials. All chemicals were of reagent grade and were used as commercially obtained. Compound $\{Fe_2(CO)_6[\mu\text{-}S_2C_6H_2(OH)_2]\}$ (**1**) was obtained according to a previously reported procedure.[1]

Preparation of the Substrates for AFM. 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. 100 mm x 100 mm pieces of a P-type Si (100) wafer with a resistivity of 15 Ω cm are used as substrates. A 200 nm silicon oxide SiO_2 layer is thermally growth on the Si surface. The substrate was cleaned previously at 800 ºC in air, cooled down to room temperature

Sample Preparation: 40 μl of freshly prepared 10^{-3}-10^{-6} M solutions of compound **1** in CH_2Cl_2 were drop-casted on the corresponding cleaned substrate at 20 ºC. Upon standing the solution for *ca.* 2 min. the solvent was allowed to evaporate.

Atomic Force Microscopy

Atomic 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. The images are processes using WSxM (freely downloadable SPM software from www.nanotec.es) operating at room temperature in ambient air conditions.

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[1] R. D. Adams and S. B. Miao, *Inorg Chem*, 2004, **43**, 8414-8426.

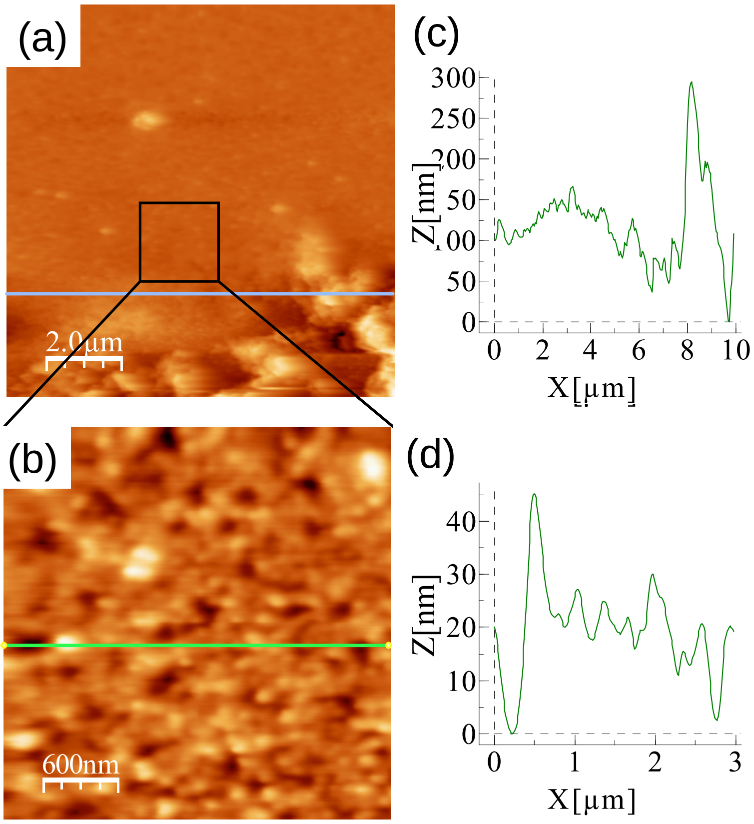

Figure S1. Large AFM topography image (a) and a zoomed area (b), and their corresponding height profiles along the lines (c,d), obtained upon adsorption of a 10^{-3} M solution of **1** in CH_2Cl_2 on a mica surface by drop casting. The images show the inhomogeneous features of the sample.

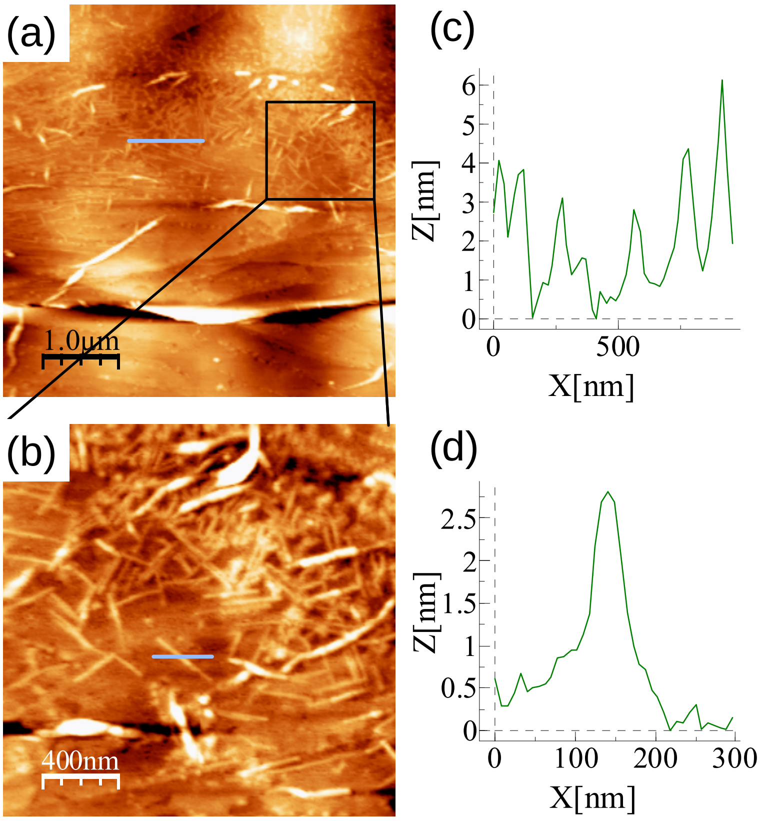

Figure S2. (a) AFM topography image resulting of the deposition of a 10^{-6} M solution of **1** in CH_2Cl_2 on a HOPG surface by drop casting. (b) A zoomed area of (a) showing features of the isolated fibres of **1**. (c) and (d) are the height profiles of the blue lines represented in the figures (a) and (b).

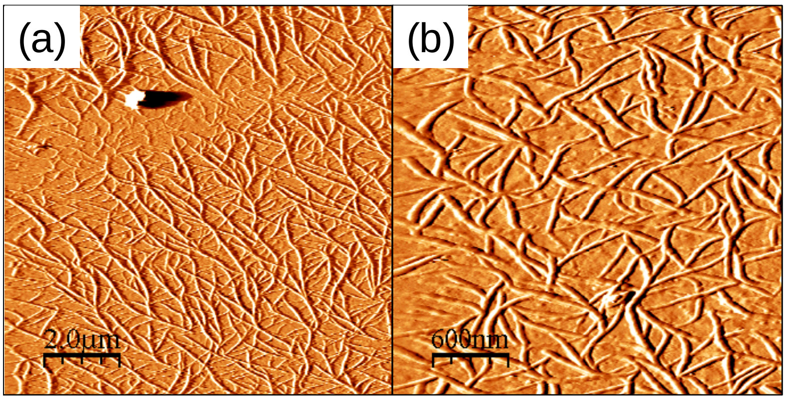

Figure S3. AFM topography images resulting of the deposition of a 10^{-5} M solution of **1** in CH_2Cl_2 on a SiO_2 surface by drop casting. (a) The image shows a large area with a very high concentration of fibres. (b) Displays a zoomed area of the image of (a) with some structural features.

Thermal Degradation of Compound 1

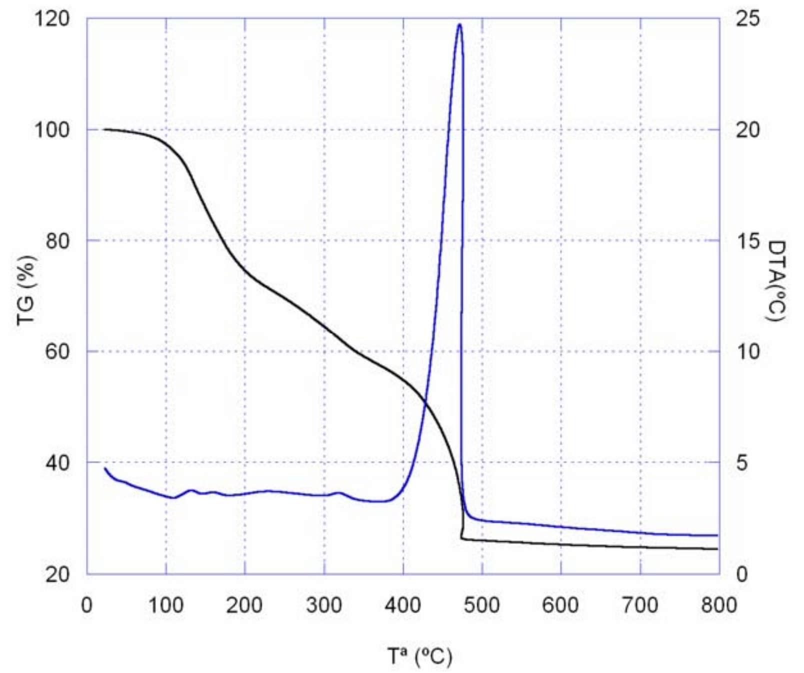

Figure S4. Thermal degradation of compound **1**, carried out in a bulk sample. Line in black corresponds to the TG while the line in blue shows the TDA. Degradation is completed at 460 ºC.

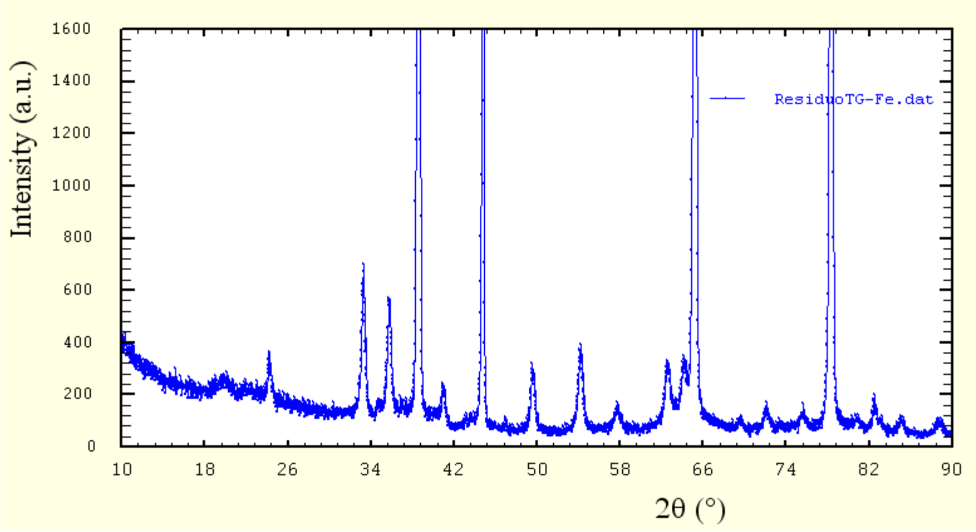

Figure S5. X-ray powder diffractogram of the solid residue obtained upon thermal degradation of compound 1. The peaks correspond to Fe_2O_3 (hematite form). The four most intense peaks are assigned to the aluminium container used for the experiment.

CVD Synthesis of SWCNTs

Synthesis of SWCNTs on surface. The entire CVD process consists of two steps: (1) catalyst precursor preparation and, (2) SWCNT growth. Syntheses were carried out by thermal CVD in a horizontal furnace with a quartz reactor tube.

1. Catalyst Precursors Preparation

(a) Standard Catalyst Precursor (used for controls). 100 mm x 100 mm pieces of SiO_2 were dipped for 10 sec in a 0.5 mM 2-propanol solution of $Fe(NO_3)_3{\cdot}9H_2O$, then it was rinsed for 2 sec in *n*-hexane and finally dried out with argon.

(b) Catalyst based on Thermal degradation of compound 1. Thermal degradation of the fibres of compound **1** obtained on SiO_2 was performed at 500 ºC under aerobic conditions for 15 min in the CVD oven.

(2) CVD Synthesis of SWCNTs. Thermal CVD synthesis was performed under a constant flow pressure. Initially, a mixture of 1500 sccm of H_2 and 200 sccm of Ar were used at 800 ºC for 20 min. to ensure the reduction of iron. Subsequently, the conditions were readjusted by keeping constant the flows of H_2 and Ar and adding to this mixture 2 sccm of ethylene for 5 min. Finally, the flow of Ar and ethylene were maintained while the flow of H_2 was reduced 100 sccm every 5 min until a final flow of 200 sccm was reached. Figure S7 shows the results obtained by using 0.5 mM 2-propanol solution of $Fe(NO_3)_3{\cdot}9H_2O$ as catalyst precursor and Figure S8 using degradation of the fibres of **1** (particles obtained shown in Figure S6) as catalyst precursor.

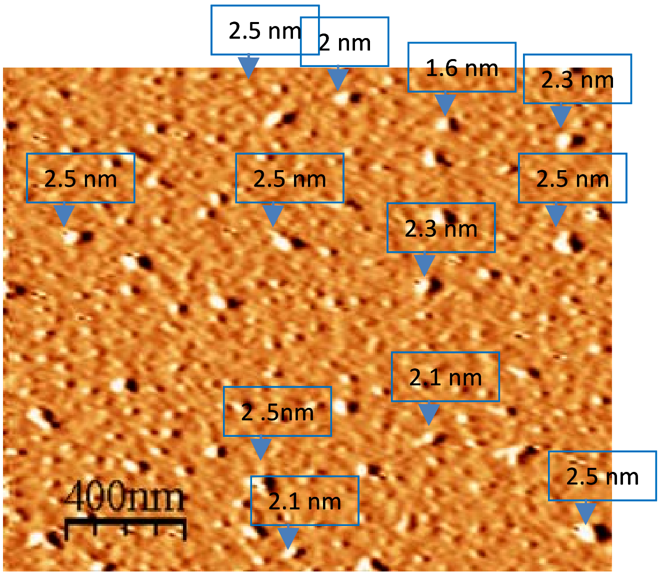

Figure S6. AFM image of the thermal degradation of the fibres of **1** on SiO_2 and details of the homogeneous heights distribution.

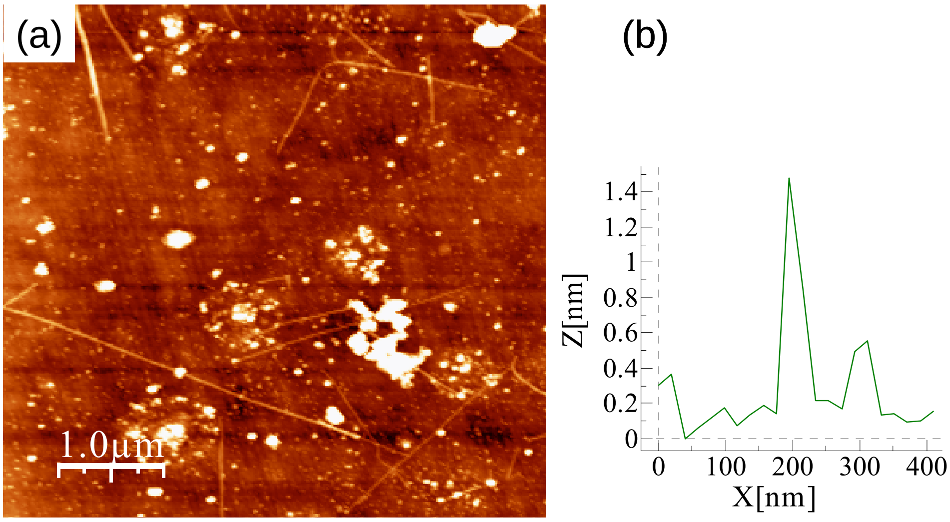

Figure S7. AFM topography images of SWCNTs grown on SiO_2 substrate by CVD at 800 ºC using $Fe(NO_3)_3·9H_2O$ (0.5 mM in 2-propanol) as catalyst precursor.

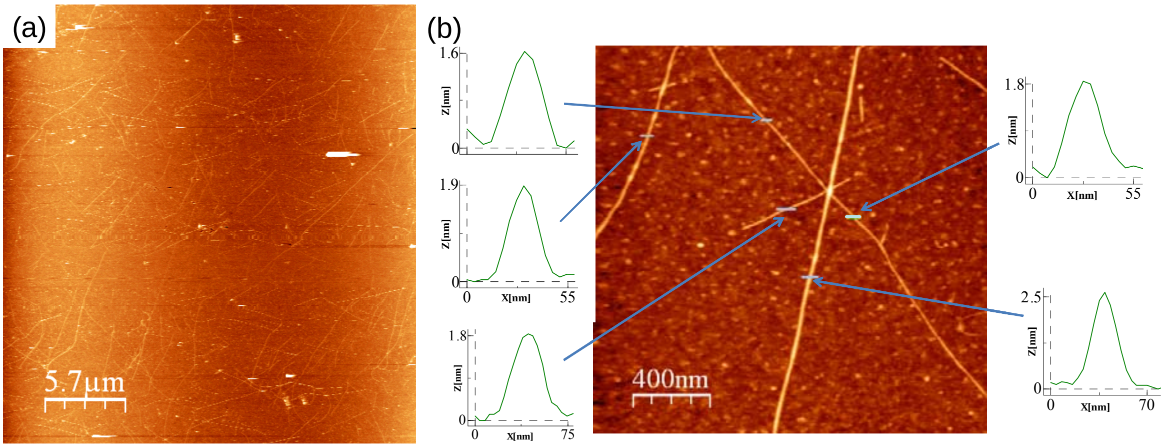

Figure S8. (a) Large area AFM image showing high density coverage of over micron-length SWCNTs. (b) AFM image showing some features of SWCNTs, including a SWCNT junction. The blue lines represented in (b) across the SWCNTs correspond to their height profiles which are in agreement with those expected for single-walled tubes.