Supporting Information

Spin State Dependence of Electrical Conductivity in Spin Crossover Materials

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Experimental details

Synthesis. All the chemicals and solvents were obtained from Sigma Aldrich and used without any further purification. Bulk powder of $[Fe(H\text{-}trz)_2(trz)](BF_4)$ **C1** was obtained following the method described previously by *Kröber et al.*[S1] Sample **C2** was synthesized in a similar way in presence of HBF_4 in the solution (2 wt%). Sample **C3** was obtained by an original method from a ligand melt: $Fe(BF_4)_2\cdot 6H_2O$ (20 mg) and 1-H-1,2,4-triazole (1 g) were mixed, rapidly heated to 130 ^oC and stirred for 1 min. Then, this melt was left to cool down to room temperature. Violet crude was solved in absolute ethanol (15 ml), centrifuged and the precipitate of the complex was washed and separated again.

Electrical conductivity measurements. The dc conductivity measurements have been performed in two-probe geometry. The powders of **C1** and **C2** (~0.2 mm thickness) were contained in a Teflon sample holder between two stainless steel electrodes (diameter 10 mm). The particles of **C3** have been dispersed in ethanol and deposited on the electrode by spin-coating. The dc electrical conductivity has been recorded in helium gas atmosphere using a TSCII SETARAM instrument[S2] in both heating and cooling modes at a rate of 2 K/min, under a bias voltage of 5 V for the samples **C1** and **C2** and of 0.5 V for the sample **C3**.

Raman spectroscopy. Raman spectra were acquired using a Labram-HR (Horiba Jobin Yvon) Raman spectrometer (600 mm^{-1} grating, 100 µm entrance slit, ~3 cm^{-1} spectral resolution) coupled to a Peltier-cooled CCD detector (Andor DU420) and an Olympus BXFM optical microscope. Raman scattering was excited at 632.8 nm by means of a HeNe laser with 0.1 mW excitation power on the sample. The laser beam was focused on the sample via a long-working-distance ×50 microscope objective (numerical aperture, NA = 0.5), which served also to collect the scattered photons. The Rayleigh scattering was removed by a holographic notch filter and the Raman spectra were recorded between 80 and 3500 cm^{-1}. For variable temperature measurements the sample was placed on the heating block of a Linkam THMS600 stage. Before the Raman measurements the samples were dehydrated at 120 °C under nitrogen flow.

IR spectroscopy. IR spectra were recorded with a Perkin Elmer Spectrum 100 spectrometer in attenuated total reflectance (ATR) mode in ambient conditions.

Atomic Force Microscopy (AFM). Surface topography images of the deposited nanoparticles of **C3** were obtained in ambient conditions using a Nanonics MV2000 atomic force microscope in intermittent contact mode. AFM image processing was carried out using the WSXM software.[S3]

Variable temperature optical reflectance measurements. The studied complexes exhibit a thermochromism suitable for optical detection. The major thermal hysteresis loops have been thus determined by diffuse reflectivity detection using an Olympus BX51 optical microscope (in dark field, reflected light mode) equipped with a CCD camera (Andor Technology, Ikon-M). The light source was a halogen lamp fitted with a 550 ± 25 nm band pass filter. The temperature was changed at a rate of 2 K/min in the heating and cooling modes by means of a Linkam THMS600 variable temperature stage. Before the measurements the samples were dehydrated at 120 °C under nitrogen flow.

Scanning Electron Microscopy (SEM). SEM micrographs were recorded using a Hitachi S4800 microscope, operating at 15 kV.

Transmission Electron Microscopy analysis. TEM micrographs were recorded using a JEOL JEM-1010 instrument (accelerating voltage of 100 kV). TEM samples were prepared by placing on a carbon coated copper grid a drop of the solid state samples dispersed in ethanol. Systematically, several images were taken at different places of each sample to test the sample homogeneity.

Mössbauer spectroscopy. ^{57}Fe Mössbauer spectra of the compound **C1** were recorded in both the HS and LS states (at 415 and 300 K, respectively) using a flow-type liquid nitrogen cryostat and a conventional constant acceleration type Mössbauer spectrometer. γ-rays were provided by a ^{57}Co(Rh) source (ca. 20 mCi). The spectrum evaluations were done with the assumption of Lorentzian line shapes using the Recoil software.[S4] All isomer shifts are given relative to α-Fe at room temperature.

X-Ray crystallography. The pXRD patterns of the samples have been recorded at room temperature using a Panalytical MPD XPert Pro powder diffractometer. For **C1**, variable temperature powder diffractograms were recorded between room temperature and 420 K using an Antoon Paar TTK 450 Chamber.

References

[S1] J. Kröber, J. P. Audiere, R. Claude, E. Codjovi, O. Kahn, J. G. Haasnoot, F. Groliere, C. Jay, A. Bousseksou, J. Linares, F. Varret, and A. Gonthiervassal, *Chemistry of Materials* **6** (1994) 1404.
[S2] J. Menegotto, P. Demont, and C. Lacabanne, *Polymer* **42** (2001) 4375.

[S3] I. Horcas, et al. *Rev. Sci. Instrum.* **78** (2007) 013705.

[S4] http://www.isapps.ca/recoil/

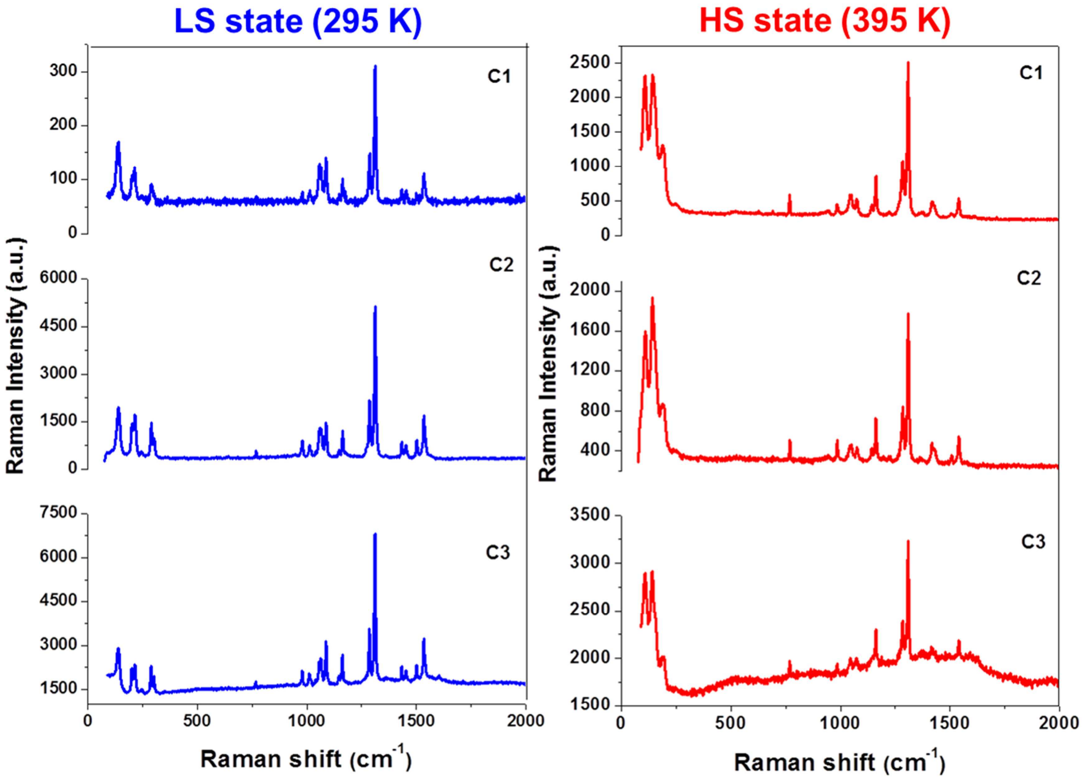

Fig. S1 Raman spectra (excited at 632.8 nm) obtained on samples **C1** - **C3**. The spectra were acquired in both the LS (left panel) and HS (right panel) states. These Raman spectra compare well with those reported in N. Ould Moussa et al. Chem. Phys. Lett. **477** (2009) 156 and in A. Urakawa, et al. *J. Phys. Chem. C* **115** (2011) 1323.

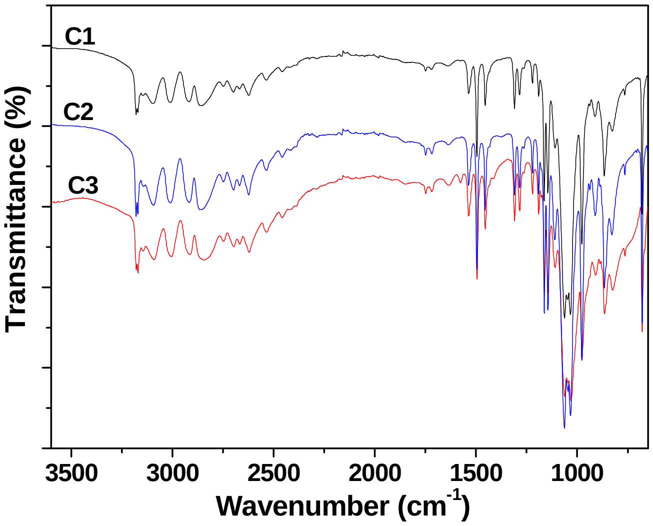

Fig. S2 IR-ATR spectra of samples **C1** - **C3**.

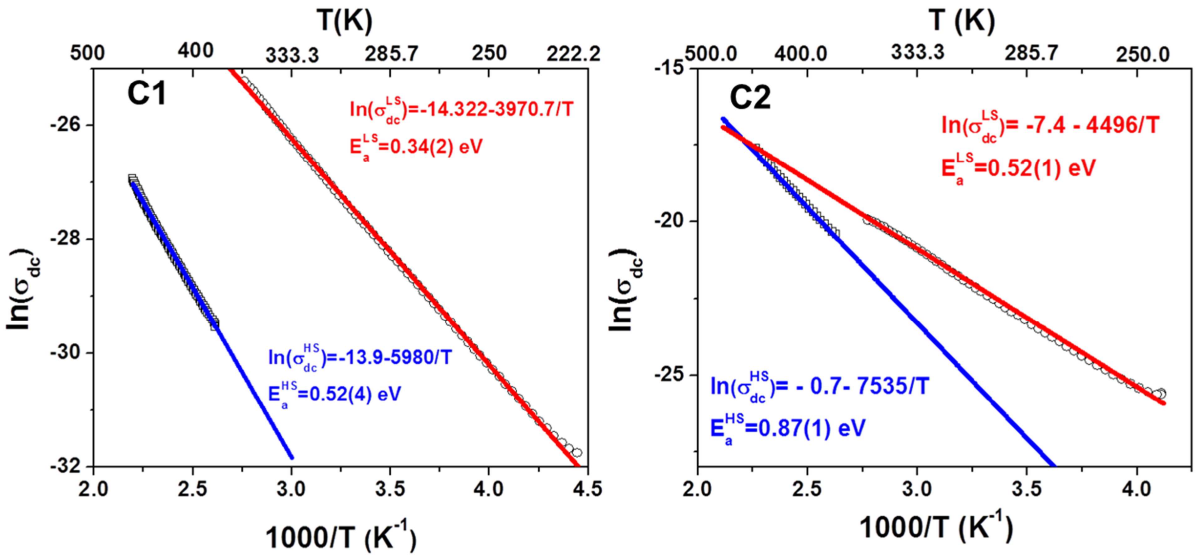

Fig. S3 Arrhenius plots of the dc conductivity for the samples **C1** (left) and **C2** (right).

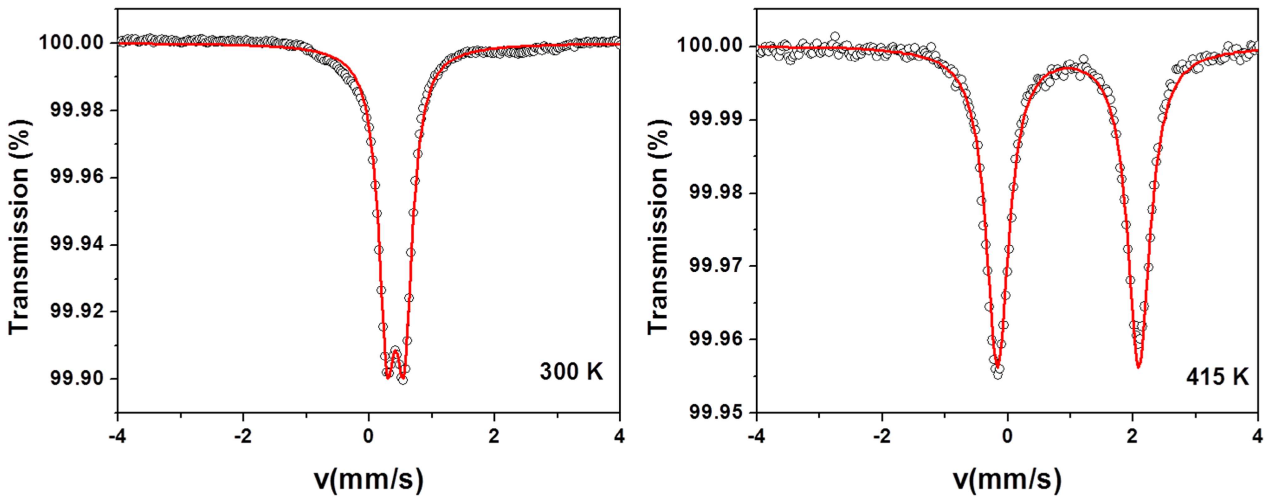

Fig. S4 ^{57}Fe Mössbauer spectra of sample **C1** recorded in the LS (left) and HS (right) states.

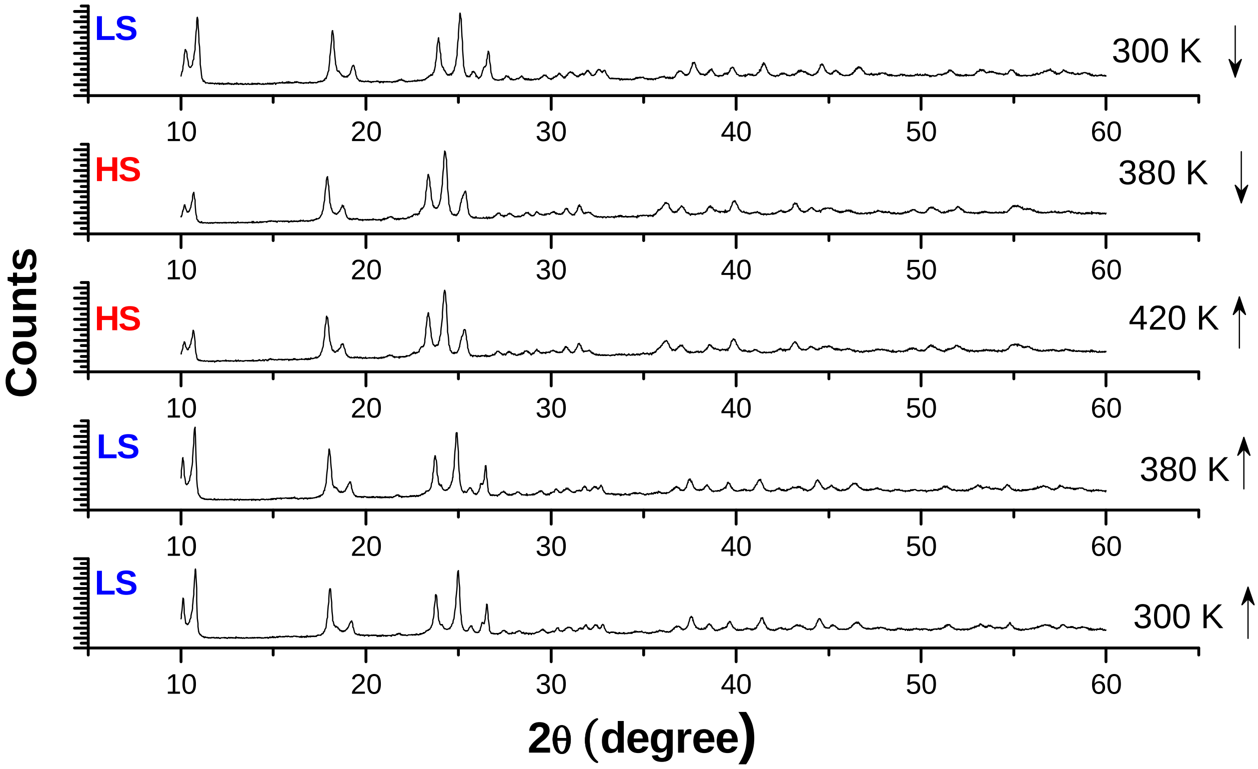

Fig. S5 XRD patterns obtained on the sample **C1**, recorded at various temperatures in both heating (↑) and cooling (↓) modes.

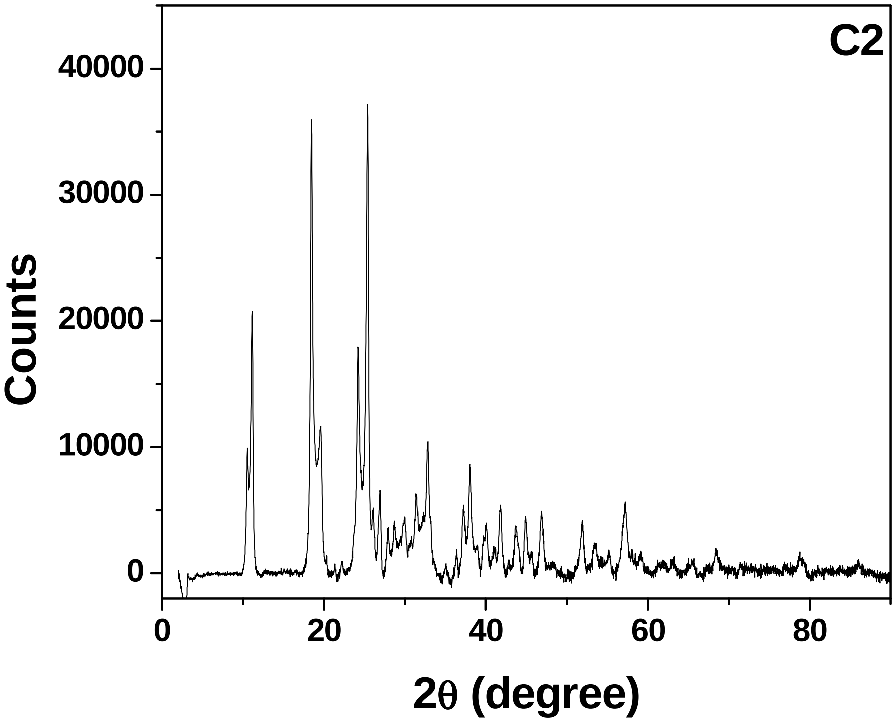

Fig. S6 XRD patterns obtained on the sample **C2** at 300K.

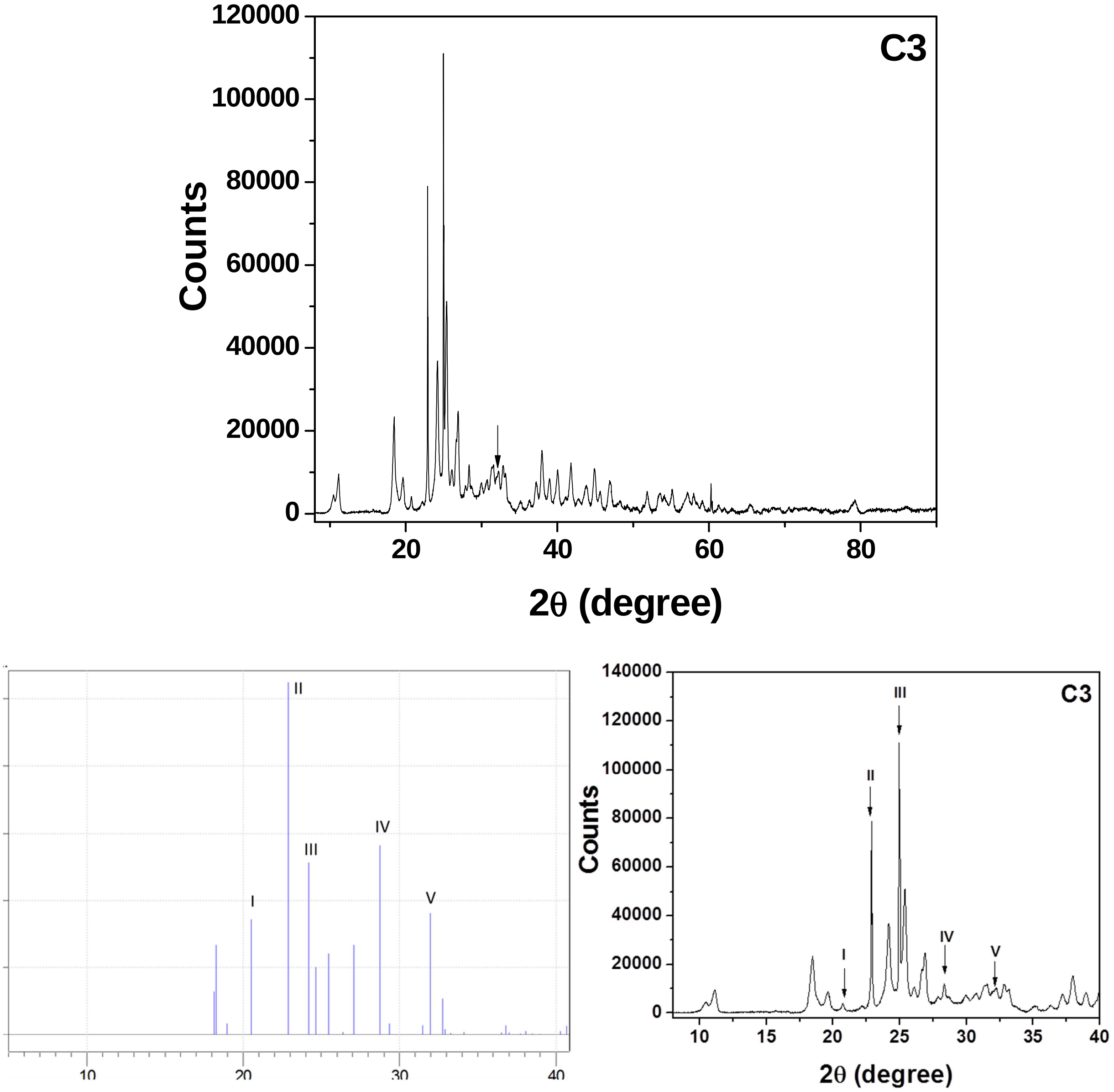

Fig. S7 (Top panel) XRD patterns obtained on the sample **C3** at 300K. (Bottom Panel) A comparison of the XRD pattern of 1-H-1,2,4-triazole generated from the single crystal structure taken from [G. A. Jeffrey, J. R. Ruble and J. H. Yates. *Acta Cryst.* (1983). B39, 388-394] with the additional peaks observed in the pattern of C3 reveals clearly the presence of a mixture of triazole with the compound [Fe(Htrz)$_2$(trz)](BF$_4$). This finding is related to the fact the C3 has been synthetized in triazole matrix.

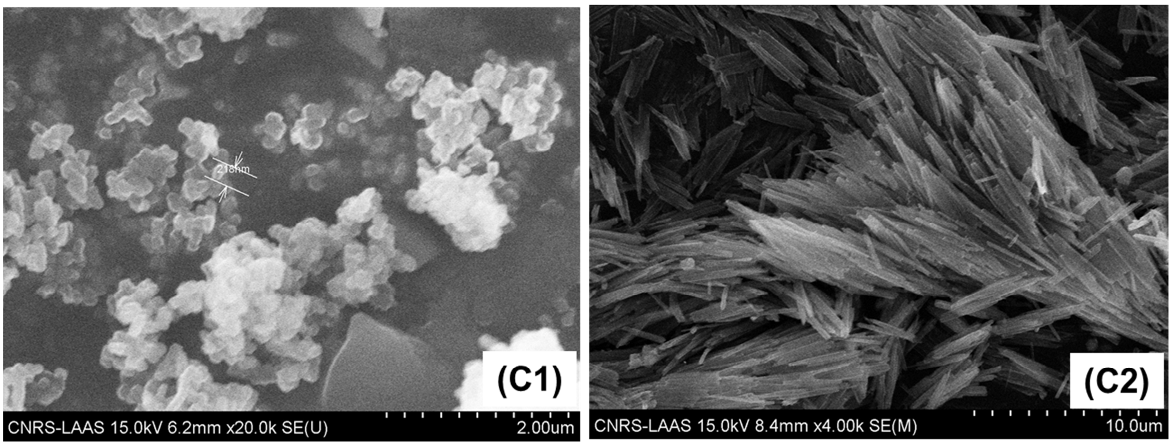

Fig. S8 Selected SEM images of samples **C1** and **C2**

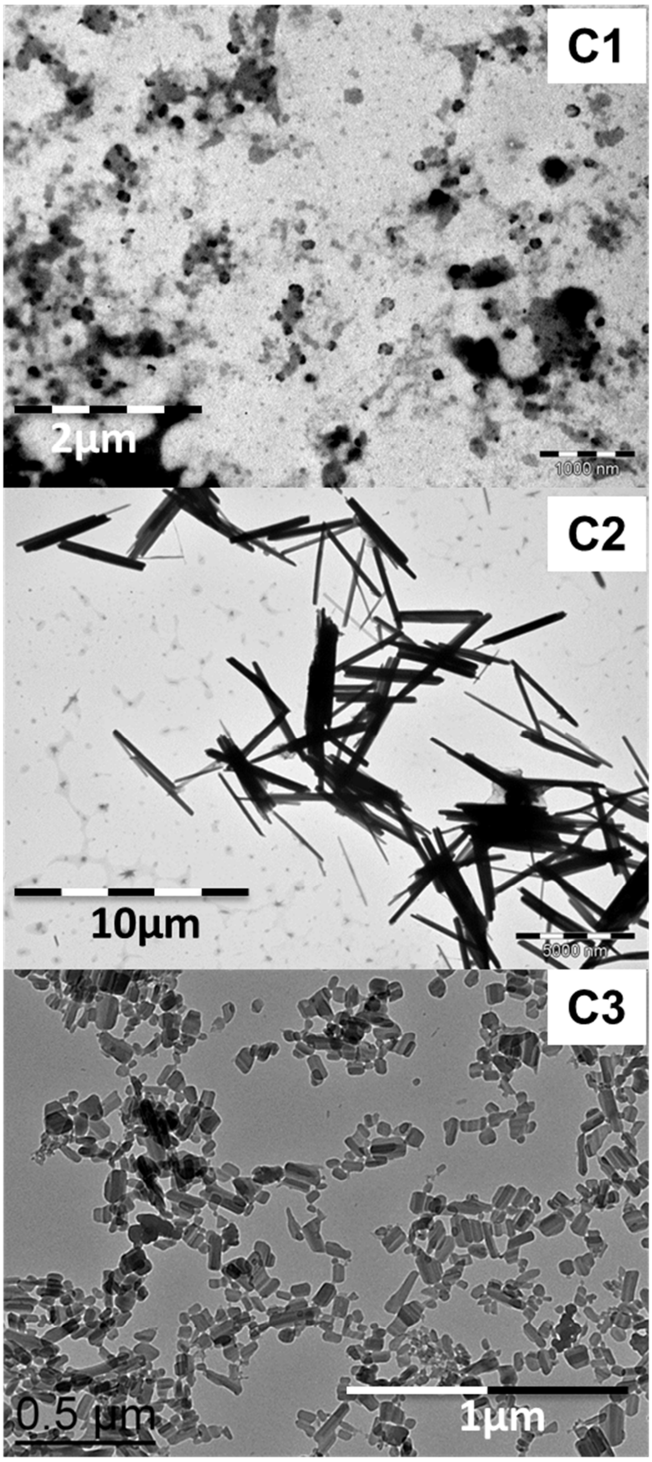

Fig. S9 Selected TEM images of samples **C1** – **C3**

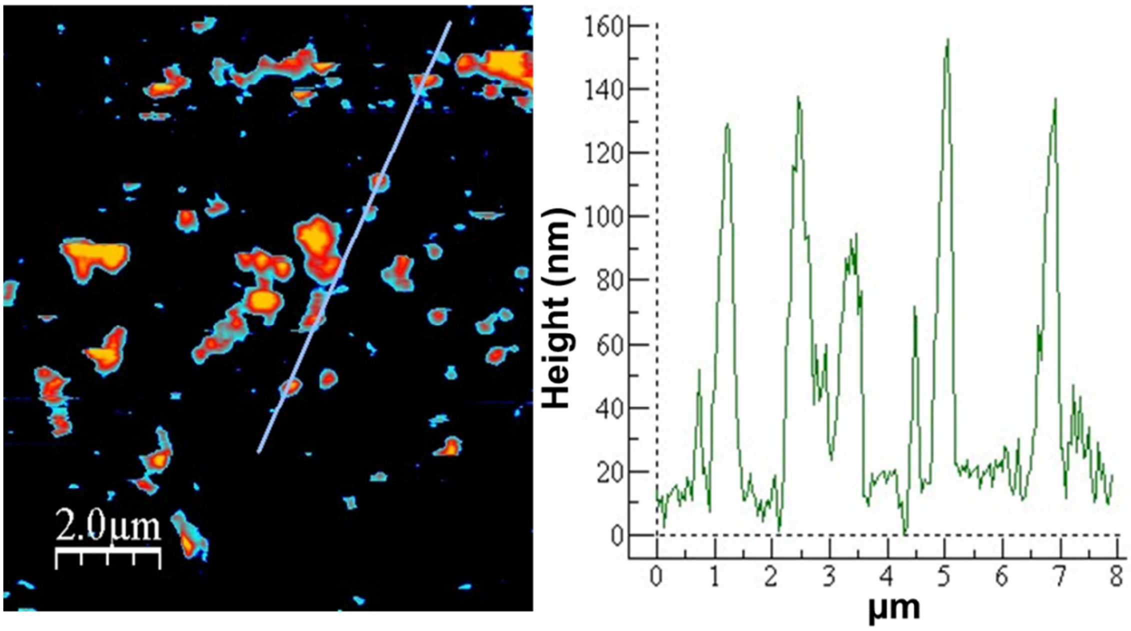

Fig. S10 AFM image of sample **C3** as deposited on the electrode surface.