Electronic Supporting Information

Sample preparation.

The structure of CoPOM and ZnPOM have been previously reported.[1] The complexes used in this work have been synthesized using the procedure described for the analogous MnII compound but using $Co(SO_4)$ and $Zn(SO_4)$ instead of $Mn(SO_4)$.[2]

HiPCo SWNTs were purchased from Carbon Inc. and purified by the gas phase method.[3]

All the solutions were prepared using Millipore water. Functionalisation of pNTs by MPOM (M = Co^{II} or Zn^{II}) was achieved as follows: 2 mg of pNTs were added to 7.5mL of a 5.10^{-3}M solution of MPOM in a 10^{-2} M dichloroacetic acid buffer whose pH has been previously adjusted to 2 by adding dilute sodium hydroxide dropwise. The mixture was stirred in an ultrasonic bath for 20 hours while maintaining the temperature of the bath below 12 °C to prevent damaging of the pNTs. This led to a dark suspension that was subsequently centrifugated under 14 000 g for 20 minutes. The supernatant was isolated, filtered on a nanoporous membrane and washed with water, giving rise to a grey glassy mat of MPOM@NTs. The sediments could be redispersed in pure water and after centrifugation, the supernatant led to identical grey glassy mats.

XPS, Raman and magnetization measurements samples were obtained by filtering the supernatant resulting of the centrifugation of the black aqueous MPOM-NTs suspensions on nanoporous membranes. For the electron microscopy experiments, the supernatant was first filtered on a nanoporous membrane, washed with water and redispersed in a minimum amount of water. Eventually, a few drops of this suspension were cast on carbon lacey grids.

XPS

XPS measurements were performed on an ESCALAB 220i XL spectrometer (Thermofisher Scientific society). The X-ray source used is the non-monochromatic ray Kα1,2 of aluminium (1486.6 eV). The beam section is around 6-7 mm2. The pass energy (CAE mode) is 20 eV for detail spectra and 100 eV for survey spectra. The spectrometer is calibrated in energy to the silver Fermi level (0 eV) and to the 3d5/2 electronic level of silver (368.3 eV). The low pressure in the analysis chamber (10-10 mbar) allows to avoid the collisions between the photoelectrons and residual gas atoms and the contamination in-situ of the sample surface. The data processing and deconvolution of photoelectron peaks were done by AVANTAGE packages supplied with the instrument.

Electrochemistry studies.

For cyclic voltammetry experiments, the source, mounting and polishing of the glassy carbon (GC, Le Carbone Lorraine, France) electrodes has been described previously.[4] A modified electrode was fabricated by depositing a few µl of the CoPOM@NTs suspension in water on a polished glassy carbon surface (GC), drying in air at room temperature, then covering with few µl of 5 wt % Nafion solution and again drying in air at room temperature. The electrochemical set-up was an EG & G 273 A driven by a PC with the M270 software. Potentials are measured against a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. Pure water from a RiOs 8 unit followed by a Millipore-Q Academic purification set was used throughout. The solutions were deaerated thoroughly for at least 30 minutes with pure argon and kept under a positive pressure of this gas during the experiments. The supporting electrolyte was a pH = 5 solution (0.4 M CH_3COONa + CH_3COOH). All experiments were performed at room temperature.

The first several cyclic voltammograms (CVs) with the CoPOM-NT-modified electrodes show a chemically reversible surface wave located slightly negative of 0.0 vs. SCE when these electrodes were fabricated with as-prepared CoPOM-NT without further washing. The current intensity of this wave substantially decreased upon subsequent runs , but the wave does not completely disappear during the present experiments. The presence of this wave might be due to slow decomposition of CoPOM after several days ageing of the complex during the grafting process. It must be pointed out that the presence of this wave did not alter the voltammetric pattern discussed throughout this paper. For clarity, the redox processes of the W-centers and the Co-center are described separately in the pH = 5 medium (0.4 M CH_3COONa + CH_3COOH). As a matter of fact, the redox activity domain of the tungsten framework is usually well separated from that of the Co-substituents in analogous molecules.[5] The cyclic voltammogram of CoPOM freely diffusing in the solution displays closely spaced W-reduction-waves, associated, on potential reversal, with two largely separated oxidation waves (Fig. 6). Such behavior was observed previously for the W-waves of the analogous complex $[Co(H_2O)_2(g\text{-}SiW_{10}O_{35})_2]^{10-}$,[5] and found to strongly depend on the acid-base properties of the intermediate reduced species. The peak current intensities of CVs obtained with CoPOM-NT-modified electrodes vary linearly with the scan rate (at least up to 1 V s-1), thus confirming the surface-confined character of these waves.[6]

The phenomena observed in the positive potential domain are shown in Figure S4. This Figure compares the voltammograms of CoPOM@NTs-modified electrode used in the pure pH = 5 electrolyte; and of the polished GC electrode in the presence of CoPOM freely diffusing in the solution. This comparison reveals an oxidation process for the Co^{2+} centre. It is worth pointing out the usual difficulty to cleanly characterise Co^{2+} centres of polyoxometalates by electrochemistry. To our knowledge, very few examples of detection of electroactivity of Co^{2+} centres as addenda atoms or hetero atom substituents in POM chemistry have been described. They concern monosubstituted POMs, $[Co^{II}W_{12}O_{40}]^{6-}$ and very recently, for the first time, some multisubstituted POMs.[5-11]

Raman Studies

Experimental details of the resonant Raman analysis.

Raman spectra were collected on a T64000 Jobin-Yvon triple spectrometer, accessorized with an optical microscope, using an Ar laser as the excitation source. The spot size was 2 µm. The pNTs sample was prepared by filtering a freshly sonicated dispersion of purified nanotubes on PTFE nanoporous membranes. For each sample, four spectra were recorded at 488.0, 514.5, 568.2 and 647.1 nm excitation wavelengths, in two distinct points of the sample. The excitation power was set up in between 0.3 and 0.7 mW to limit heating of the samples. The room temperature was stabilized at 23 °C. The spectra were calibrated using a silicon wafer prior to each acquisition. Normalisation was done by dividing the crude intensity by the irradiation power and the acquisition time. The RBM areas were simulated using Lorentzian line shapes with linewidth within the 7-10 cm^{-1} range. The peaks were attributed to each chirality using Kataura plots calculated by the “extended tight binding+many body effect” model. [12]

SERS experiment.

The spot size was 1-2 µm depending on the objective lens used. The 514.5 nm radiation from an Ar-Kr laser was used as excitation wavelength. Silver colloids were prepared by reducing

$AgNO_3$ by $NaBH_4$. The obtained surfaces were similar to the ones previously reported by our group.[13]

Supporting figures and tables

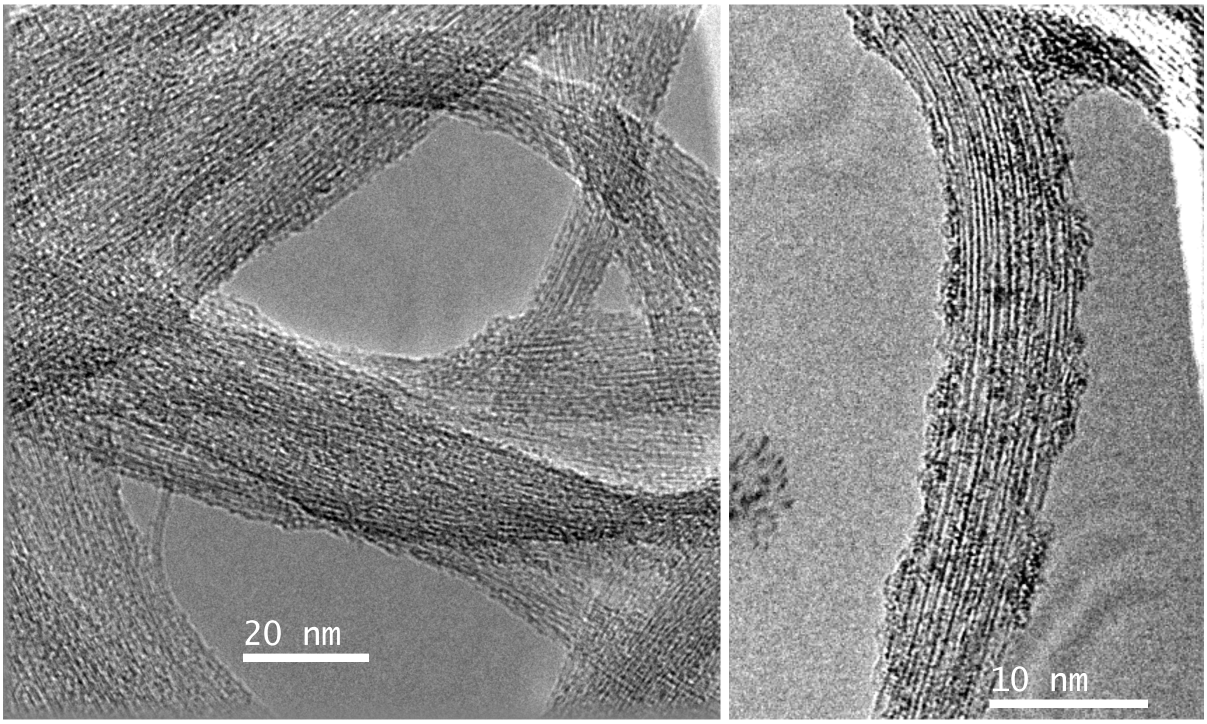

Figure S1: TEM image of pNTs (left, scale bar: 20 nm) and HRTEM image of CoPOM@NTs (right, scale bar: 10 nm)

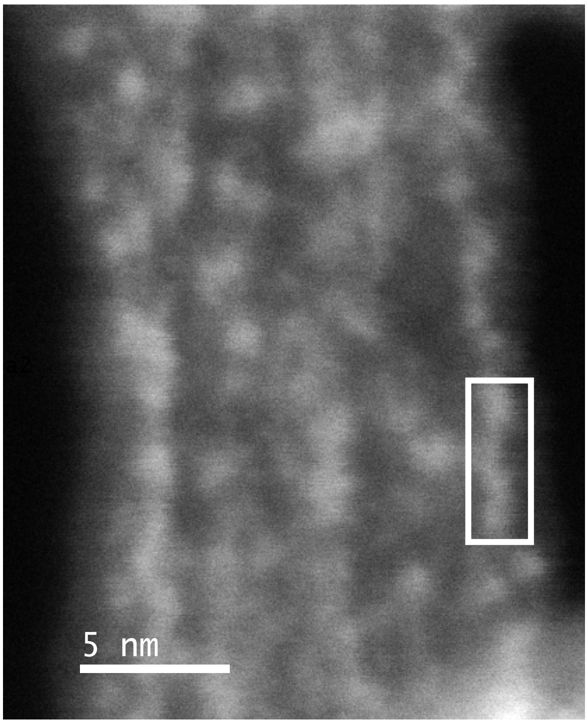

Figure S2: HAADF-STEM image of CoPOM@NTs at high magnification (scale bar: 5 nm) and inset area corresponding to the EELS spectrum displayed in Fig. 3.

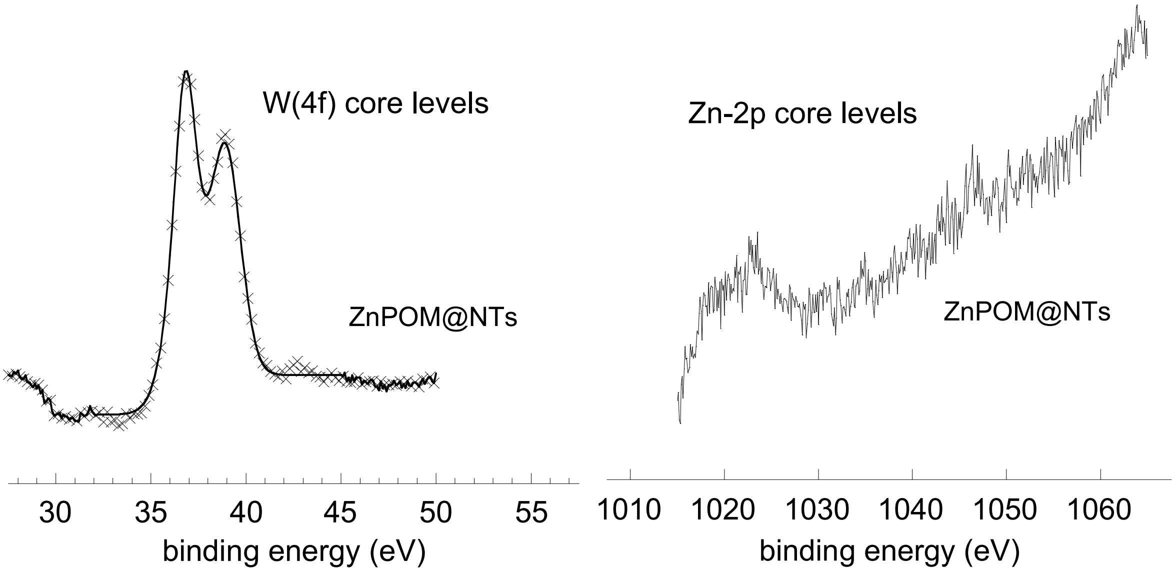

Figure S3: XPS spectra of ZnPOM@NTs focused on the W(4f) and Zn(2p) core levels.

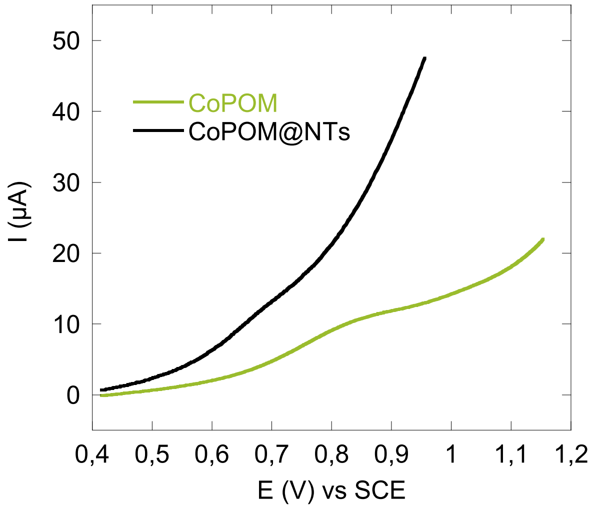

Figure S4: Voltammograms restricted to the Co-electroactivity domain of CoPOM@NTs-modified electrode and CoPOM deposited on a glassy carbon electrode. The reference electrode was a KCl saturated calomel electrode (SCE) and the counterelectrode a platinum gauze of large surface area. The scan rate was 10 mV s^{-1}.

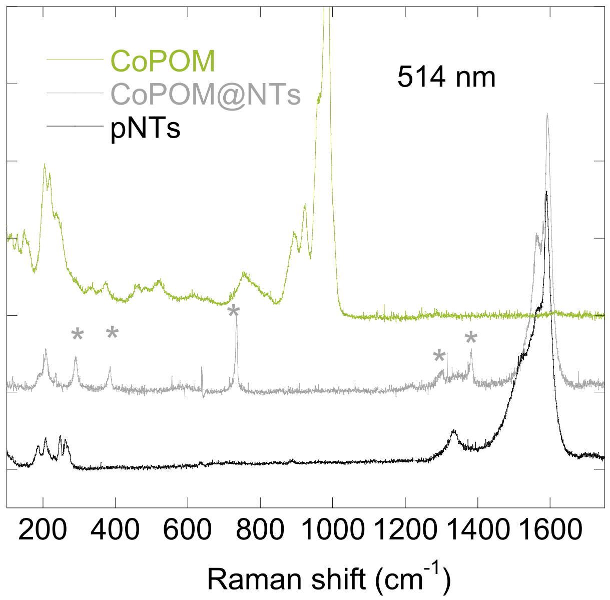

Figure S5 : Raman spectra of the pNTs, CoPOM@NTs and CoPOM molecule recorded under irradiation at 514 nm. The stars indicate resonances from the filter used as a support.

Co POM	CoPOM@NTs	calculated[14]	experimental[15]	Assignment
1099	1076	1066	1080 IR	ν_{as}(W-O$_t$), ν_{as}(W-O$_{2c2}$-W)
989	956	998 987	1004 R 993 R	ν_s(W-O$_t$), ν_{as}(W-O$_t$),
968		981	986 R	ν_{as}(W-O$_t$),
909		927 915	925 R 898 R	ν_{as}(W-O$_t$), ν_{as}(W-O$_{2c1}$-W), ν_{as}(W-O$_{2c2}$-W),
 780	848 757	840	790 R[16]	ν_{as}(W-O$_{2c1}$-W)
	542		539 R[17]	ν Co-O
570	648	530 521	523 R 518 R	ν_s(W-O$_{2c1}$-W), δ(W-O$_{2c1}$-W) δ(W-O$_{2c1}$-W), δ(W-O$_{2c2}$-W)
453	481 434 384	466 446	474 R 433 R	δ(W-O$_{2c1}$-W), δ(W-O$_{2c2}$-W) δ(W-O$_{2c1}$-W)

Table S1 : Observed vibrational frequencies, reference values (in cm^{-1}) and assignments for CoPOM and CoPOM@NTs systems. IR and R indicate IR and Raman active vibrations respectively. Vibrations have been named after the nomenclature proposed by Bridgeman.[14]

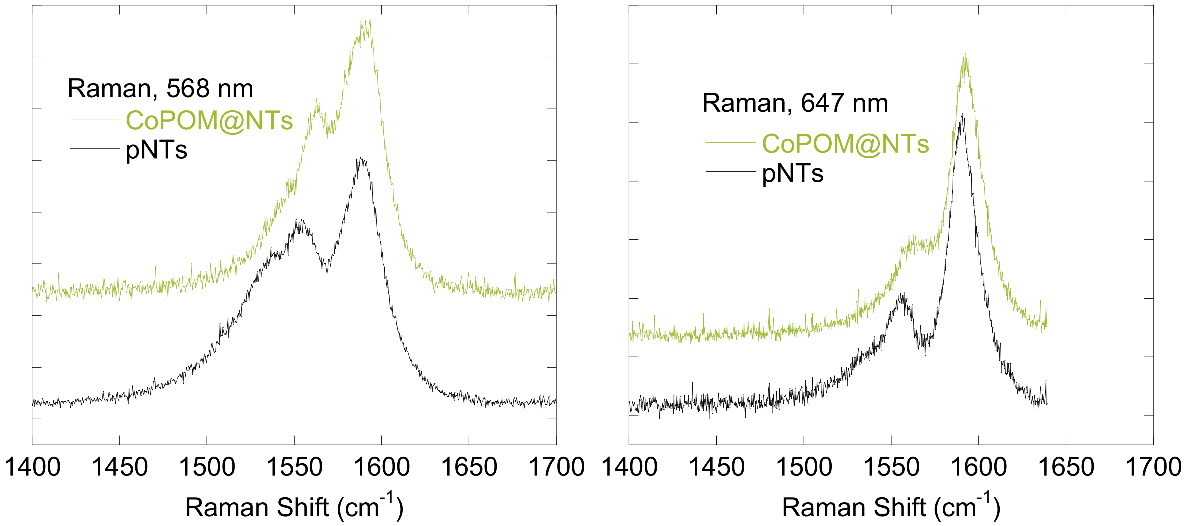

Figure S6 : Resonant Raman spectra focused on the G-mode area of pNTs and CoPOM@NTs under irradiation at 568 and 647 nm.

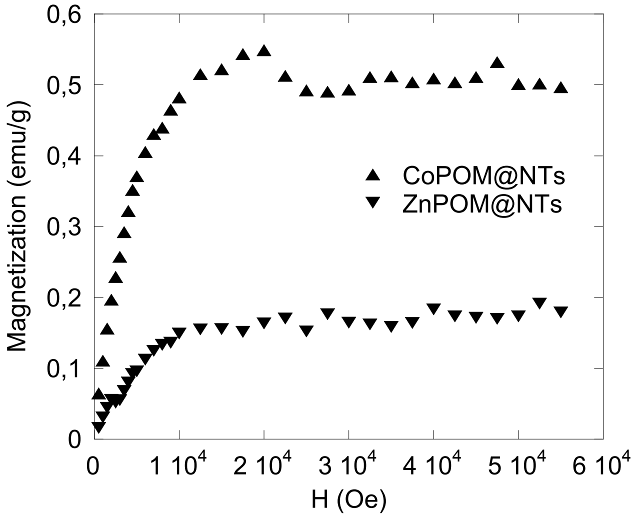

Figure S7: Magnetisation vs Field plots of CoPOM@NTs and ZnPOM@NTs , recorded at 2K on a sample prepared from a different batch of purified nanotubes.

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