Supporting information

Single-walled carbon nanotubes as nano-electrode and nano-reactor to control the pathways of a redox reaction

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S1.1 Molecular modelling

Molecular models of the relative sizes and shapes of the encapsulated $Cp^{Me}Mn(CO)_3$ and a [10,10]SWNT (has the same internal diameter as an average SWNT used in this study) (figure S1) reveals that the $Cp^{Me}Mn(CO)_3$ guest fits snuggly inside the nanotube channel. The commensurate size of the nanotube and guest molecules leads to effective van der Waals interactions between the two species and prevents the guest molecules from leaving the nanotube.

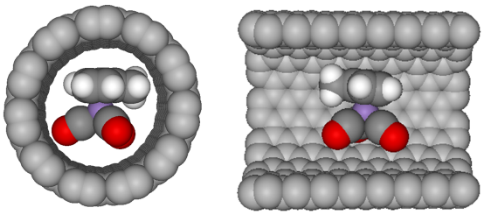

Figure S1. Molecular diagram showing the relative van de Waals radii of $Cp^{Me}Mn(CO)_3$ and the [10,10]SWNT, demonstrating the commensurate size of the [10,10]SWNT and the $Cp^{Me}Mn(CO)_3$.

The commensurate size of the guest and [10,10]SWNT also prevents diffusion of solvent molecules along the nanotube channel as there is insufficient space between the guest and nanotube sidewall for the solvent molecules to pass through (figure S2).

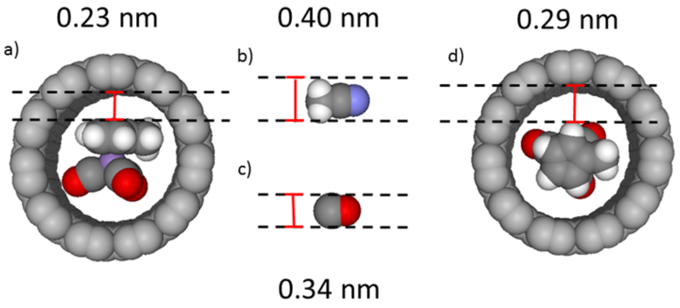

Figure S2. Molecular diagram showing the relative van der Waals radii of a) $Cp^{Me}Mn(CO)_3$@[10,10]SWNT b) acetonitrile c) CO and d) an alternate orientation of $Cp^{Me}Mn(CO)_3$@[10,10]SWNT. This demonstrates that the critical van der Waals size and shape of acetonitrile and CO are too large to fit between the nanotube sidewall and guest molecules preventing diffusion of solvent molecules (acetonitrile) into and eliminated CO molecules out of the nanotube.

S1.2 Solution CV of $Cp^{Me}Mn(CO)_3$ at -40 °C

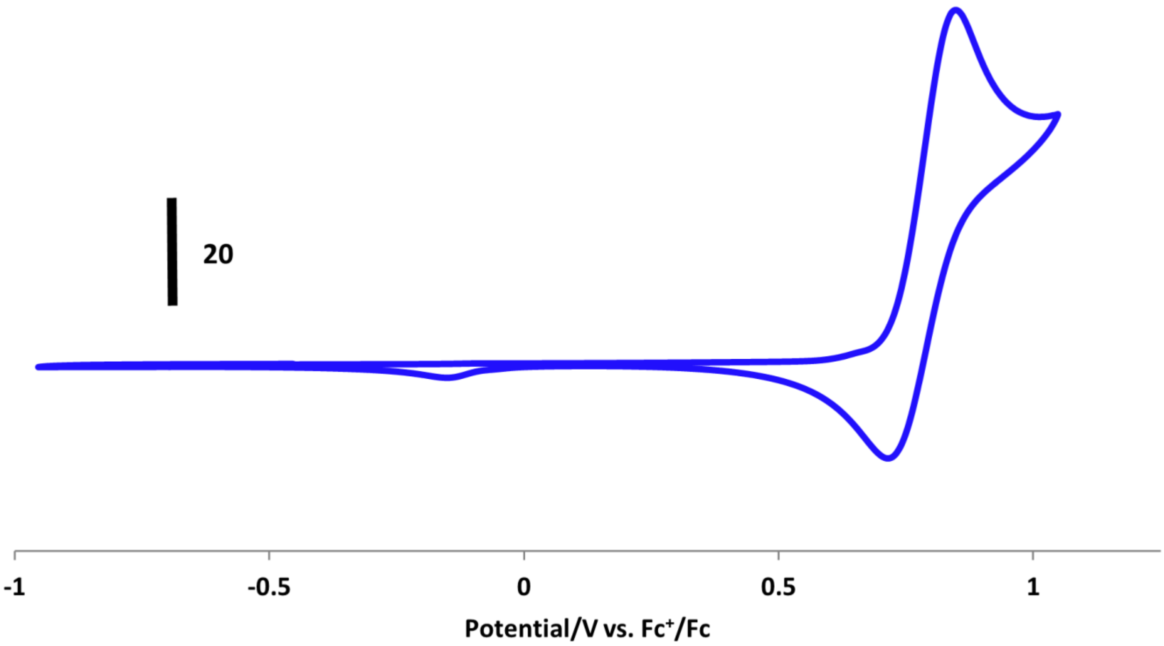

Figure S3. Cyclic voltammogram of $Cp^{Me}Mn(CO)_3$ using a GCE at -40 °C. The cyclic voltammetry experiment was performed in MeCN at 233 K containing $[N^nBu_4][BF_4]$ (0.1 M) as the supporting electrolyte at a scan rate of 100 mVs^{-1}.

The electrochemical reaction of $Cp^{Me}Mn(CO)_3$ is quasi reversible at -40 °C. The $E_{1/2}$ for this oxidation is 0.78 V (vs. Fc+/Fc).

S1.3 Calculating the surface area of the SWNT electrode

The electrochemical surface area of the electrode was calculated using the Randles-Sevcik equation (equation 1). The CV was recorded at a series of different scan rates. The peak potential was plotted against the square root of the scan rate. From the gradient of this graph the area was calculated (equation 2).

Equation 1. Randles-Sevcik equation.

$$i_p = 2.69\ x\ 10^5 n^{3/2} A D_o^{1/2} v^{1/2} C_o$$

Equation 2.

$$Gradient = \ 2.69\ x\ 10^5 n^{3/2} A D_o^{1/2} C_o$$

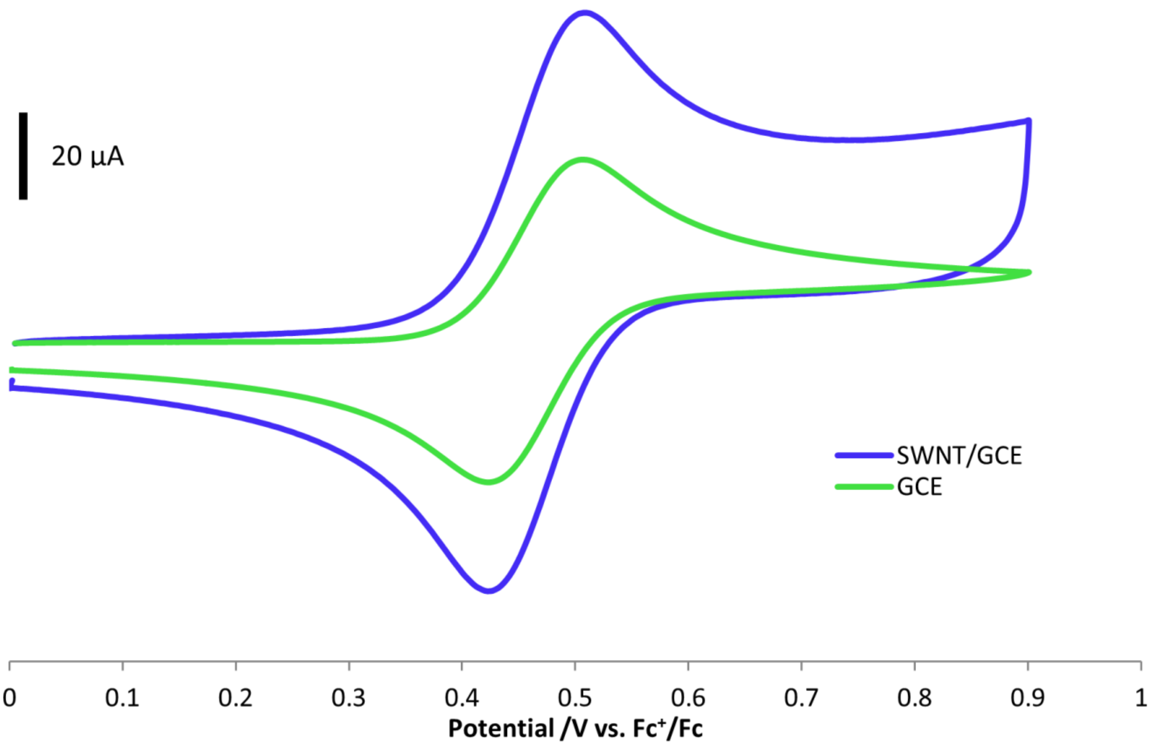

Figure S4. Cyclic voltammograms of Fc using a GCE (green) and Fc using a SWNT/GCE (blue). Both voltammograms were recorded in the same solution. The cyclic voltammetry experiments were performed in MeCN at 293 K containing $[N^nBu_4][BF_4]$ (0.1 M) as the supporting electrolyte at a scan rate of 100 mVs^{-1}.

The area of the GCE was calculated using geometric calculations (πr^2, r = 1.5 mm, A = 0.0706 cm^{-2}) and the electrochemical area was calculated using the Radles-Sevcik equation (0.0721 cm^{-2}). The electrochemical surface area of the SWNT/GCE was also calculated (A = 27.05 mm^2).

The surface area of the GCE/SWNT (0.01 mg) is 27.05 mm^2 compared to 7.21 mm^2 for the GCE. This equates to an enhancement of **375%**.

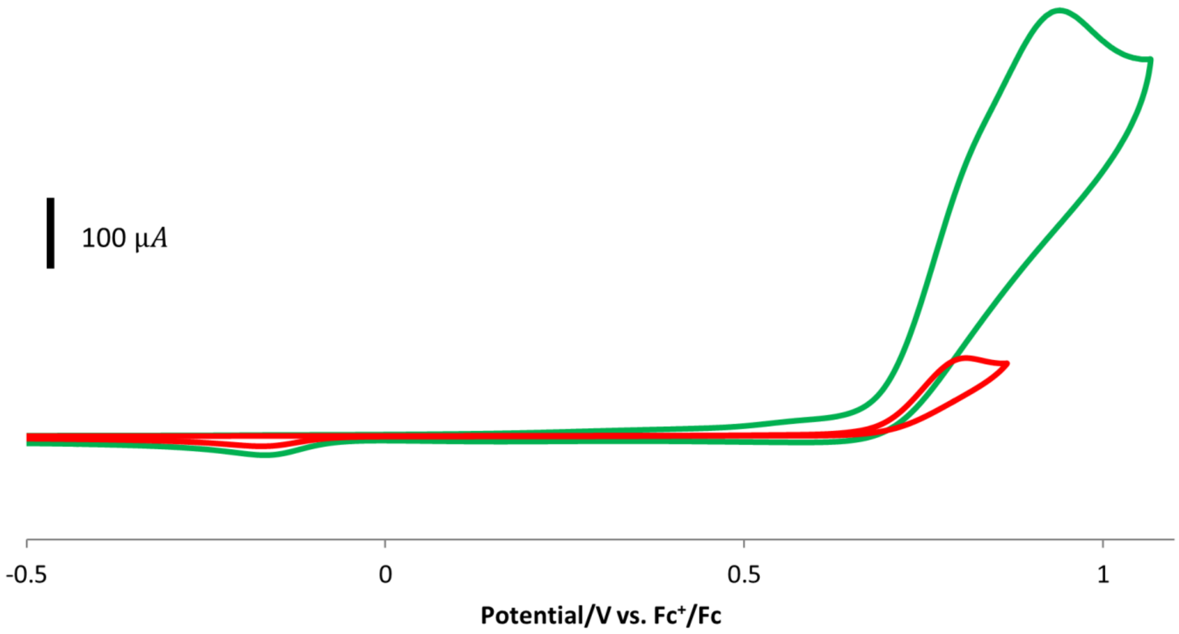

Figure S5. Cyclic voltammograms of $Cp^{Me}Mn(CO)_3$ using a GCE (red) and $Cp^{Me}Mn(CO)_3$ using a SWNT/GCE (green). Both voltammograms were recorded in the same solution. The cyclic voltammetry experiments were performed in MeCN at 293 K containing $[N^nBu_4][BF_4]$ (0.1 M) as the supporting electrolyte at a scan rate of 100 mVs^{-1}. An enhancement in current for the SWNT/GCE is observed.

A clear enhancement in current is observed when using the SWNT/GCE compared to GCE due to the increase surface area of the nanotube covered electrode.

S1.4 Calculating the number of molecules in the diffusion layer of GCE from the solution CV of $Cp^{Me}Mn(CO)_3$

Integration of the total current measured when scanning past the peak potential for the first oxidation of $Cp^{\mathbf{Me}}Mn(CO)_3$ during the CV of $Cp^{\mathbf{Me}}Mn(CO)_3$ (3 mmol, 0.1 V s^{-1}) provides the total amount of charge generated (118 mV). Using Faraday's law, the mass of molecules in the diffusion layer at this time in the experiment was calculated to be 5.78×10^{-5} mg, a factor of 38 fewer than the approximate mass of encapsulated $Cp^{\mathbf{Me}}Mn(CO)_3$ in a typical $Cp^{\mathbf{Me}}Mn(CO)_3$@SWNT electrode (0.0022 mg). The cyclic voltammetry experiment was performed in MeCN at 293 K containing $[N^nBu_4][BF_4]$ (0.1 M) as the supporting electrolyte at a scan rate of 100 mVs^{-1}, the capacitive effect have not been removed.

S1.5 Calculating the filling percentage of $Cp^{Me}Mn(CO)_3$@SWNT

Multiple methods were used to determine the filling percentage of $Cp^{Me}Mn(CO)_3$ in SWNT

S1.5.1 Geometrical considerations

The maximum filling ratio of **1**@SWNT was approximated theoretically by inserting as many $Cp^{Me}Mn(CO)_3$ molecules as possible inside a [10,10]SWNT of known length in a molecular simulation package (ViewerPro), *i.e.* the maximum number of **1** without unreasonable distortion of the molecules and nanotube considering the relative van der Waals radii. This provided a theoretical

100% filling percentage to compare against experimental samples. Thus all experimental filling values are quoted as a percentage of filling compared to this theoretical maximum packing.

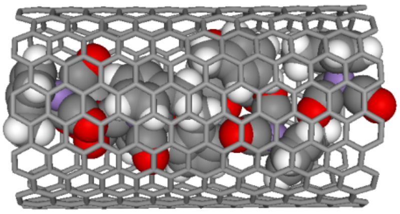

Figure S6. Molecular diagram showing the absolute maximum packing of $Cp^{Me}Mn(CO)_3$ into a [10,10]SWNT considering the relative van der Waals radii.

Maximum capacity of $Cp^{Me}Mn(CO)_3$

Number of Mn atoms in seven $Cp^{Me}Mn(CO)_3$ molecules = 7

Mass of $Cp^{Me}Mn(CO)_3$ = 218.09 g mol^{-1}

Number of carbon atoms in a [10,10]SWNT required to encapsulate seven $Cp^{Me}Mn(CO)_3$ molecules = 462

Mass of carbon required to encapsulate seven $Cp^{Me}Mn(CO)_3$ molecules = 462 x 12 = 5544 g mol^{-1}

Mass percentage of guest molecule in $Cp^{Me}Mn(CO)_3$@[10,10]SWNT sample = [(218.09 x 7)/((218.09*7)+5544] x 100 = **21.6 %**

Maximum atomic percent of Mn:C

Number of Mn atoms in seven $Cp^{Me}Mn(CO)_3$ molecules = 7

Number of carbon atoms in a [10,10]SWNT required to encapsulate seven $Cp^{Me}Mn(CO)_3$ molecules = 462

Number of carbon atoms in seven $Cp^{Me}Mn(CO)_3$ molecules = 63

Atomic percent of Mn:C = [7/(462 + 63)] x 100 = **1.33 %**

S1.5.2 Chronocoulometry

A potential (1.45 V) past the first oxidation of manganese was applied to an electrode cast with $Cp^{Me}Mn(CO)_3$@ SWNT. The charge generated over time (600 s) was recorded and this charge can be related to the number of molecules participating in the oxidation by Faraday's Law.

Equation 3. Faraday's Law

$$m = \frac{QM}{zF}$$

$m = Mass\ of\ material$
$Q = Charge$
$M = Molar\ mass$
$z = Number\ of\ electrons$
$F = Faraday\ constant$

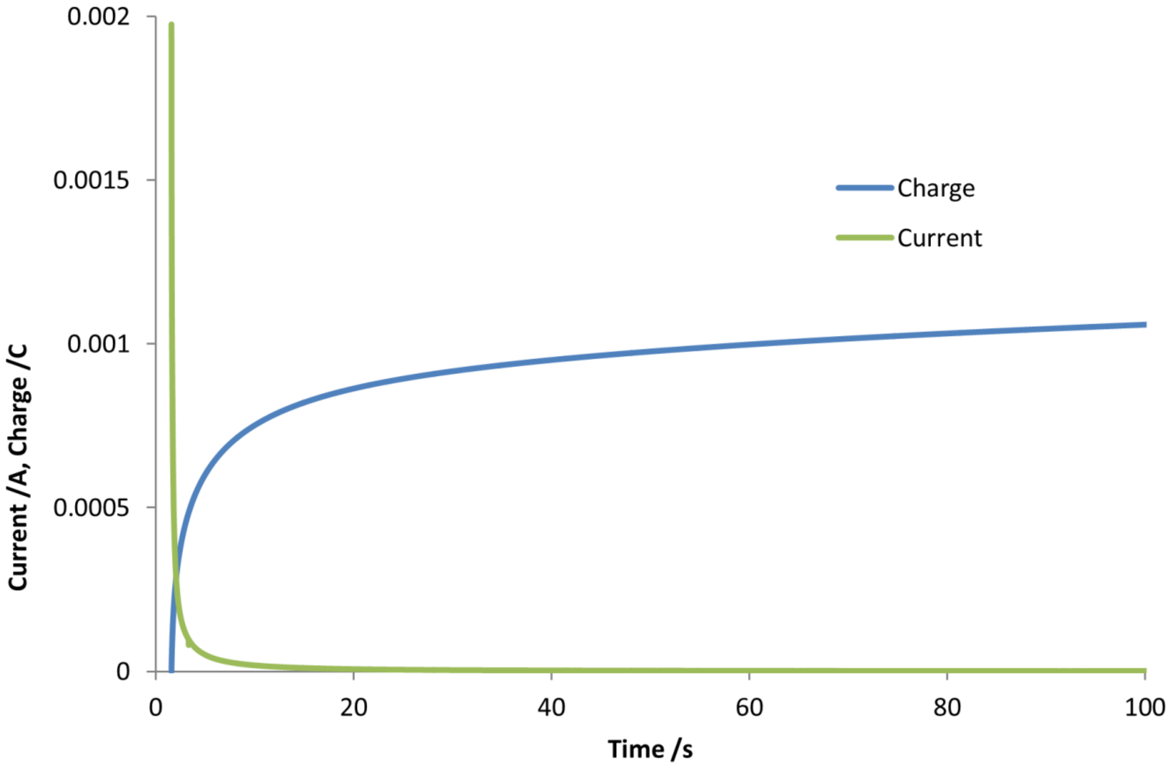

Figure S7. A plot of charge generated by $Cp^{Me}Mn(CO)_3$@ SWNT over time upon application of 1.45 V. Experiment was performed in MeCN at 293 K containing $[N^nBu_4][BF_4]$ (0.1 M) as the supporting electrolyte.

A large initial charge is observed due to the fast oxidation of encapsulated $Cp^{Me}Mn(CO)_3$ molecules in nanotubes attached to the electrode. This is followed by a steady charge increase due to solvent decomposition and other capacitance effects. The time (t) at which the charge measured starts to originate from only the solvent decomposition is approximated to be when the current is almost zero (0.00001 A). When the current drops to 0.00001 A, the charge is measured. To reduce any other contributions to charge other than electrons produced from the oxidation of $Cp^{Me}Mn(CO)_3$ the charge generated by empty nanotubes in a separate experiment is subtracted from the charge generated by $Cp^{Me}Mn(CO)_3$@ SWNT. Faraday's Law is used to calculate the mass of **1** in the **1**@SWNT material (0.01 mg) cast onto the GCE.

Table 1. Calculation performed to determine the fill percentage from chronocoulometry experiments. The calculations for the two experiments are shown (Exp 1 and Exp 2)

	Exp 1	**Exp 2**
Current drops to almost zero (0.00001 A) at t =	15.50 s	14.91s
Charge at t seconds generated by $Cp^{Me}Mn(CO)_3$@SWNT	8.26×10^{-4} C	7.30×10^{-4} C
Charge from Empty SWNT at t	5.70×10^{-5} C	5.70×10^{-5} C
Charge of $Cp^{Me}Mn(CO)_3$@SWNT minus charge of empty nanotubes	8.07×10^{-4} C	6.73×10^{-4} C
Amount of molecules contributing to the charge (from eqn. 3)	1.82×10^{-6} g	1.52×10^{-6} g
Filling percentage	**84.45 %**	**70.46 %**

1.5.3 Gravimetric analysis

The empty SWNTs were weighed prior to performing the $Cp^{Me}Mn(CO)_3$ filling experiment (section 2.1.1) using a microbalance. After filling the nanotubes are weighed again, and the difference should equate to the weight of encapsulated $Cp^{Me}Mn(CO)_3$.

Table 2. Results and percentages from gravimetric analysis. Each experiment was performed under the same conditions.

Experiment	Weight before (mg)	Weight after (mg)	Encapsulated $Cp^{Me}Mn(CO)_3$	Weight percent $Cp^{Me}Mn(CO)_3$	Filling percentage
1	5.57	6.45	0.88	13.6 %	63 %
2	5.27	6.08	0.81	13.3 %	62 %
3	11.46	13.58	2.12	15.6 %	72 %

S1.5.4 Thermogravimetric analysis (TGA)

TGA was performed to determine the percentage weight of the encapsulated $Cp^{Me}Mn(CO)_3$.

Table 3. Results and percentages from the TGA experiment. Experiment 1 and 3 were heated to 1000 °C at a rate of 10 °C min^{-1}. Experiment 2 was heated to 1000 °C at a rate of 1 °C min^{-1} All TGA experiments were performed under an atmosphere of air.

Experiment	Mass percent $Cp^{Me}Mn(CO)_3$	Total mass percent minus water	Filling percentage
1	11.55	93.24	57.61
2	9.73	94.62	47.61
3	9.11	94.31	44.72

There is a small increase in residual weight percent compared to empty SWNTs. This is potentially due to manganese oxide formation that is not further oxidised until temperatures surpassing 1000 °C.

S1.5.5 Quantitative EDX

EDX analysis was performed on suspended bundles of nanotubes of about 50 – 100 supported on an amorphous carbon film using a 100 keV electron beam. The beam was focused on a 3 nm sport using condenser aperture number 3. The atomic percent of carbon to manganese was obtained and compared to the maximum filling ratio obtained using geometric considerations.

Table 4. Table showing the atomic percent of carbon and Manganese $Cp^{Me}Mn(CO)_3@SWNT$

C (%)	Mn (%)	Ratio Mn:C
88.67	0.15	0.00169
86.05	0.15	0.00174
91.57	0.17	0.00186
91.37	0.11	0.00120

Average atomic ratio Mn:C from EDX = 0.00162 ± 0.0004

Maximum atomic ratio calculated from geometric considerations = 0.0133

Filling percentage = [0.00162/0.0133]*100 = **12.5 %**

The atomic percent of carbon is higher than expected for the sample, as the sample is suspended on an amorphous carbon film which can potentially increase the size of the carbon signal.

1.5.6 TEM extrapolation approximation

High resolution transmission electron microscopy (HRTEM) of $Cp^{Me}Mn(CO)_3@SWNT$ confirms the successful encapsulation of the Mn guest complex with metallic nanoparticles observed in the interior of the SWNTs as a result of decomposition of the guest under the high energy electron beam. The nanoparticles are estimated to be between 20-50 metal atoms. Counting the nanoparticles per length of tube, considering the number of metal atoms in a nanoparticle and comparing with the maximum packing of $Cp^{Me}Mn(CO)_3$ per length tube in the model allows an estimation of the filling percentage.

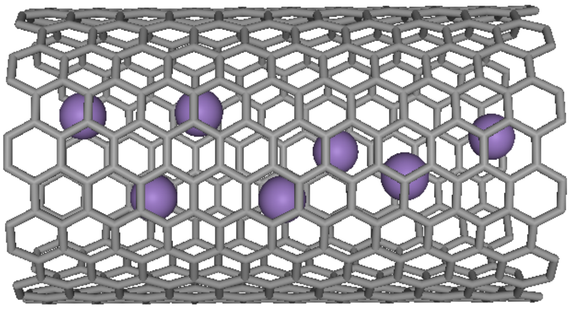

Figure S8. Molecular diagram showing the maximum packing of $CpMeMn(CO)_3$ in a nanotube of length 2.53 nm with the ligands removed.

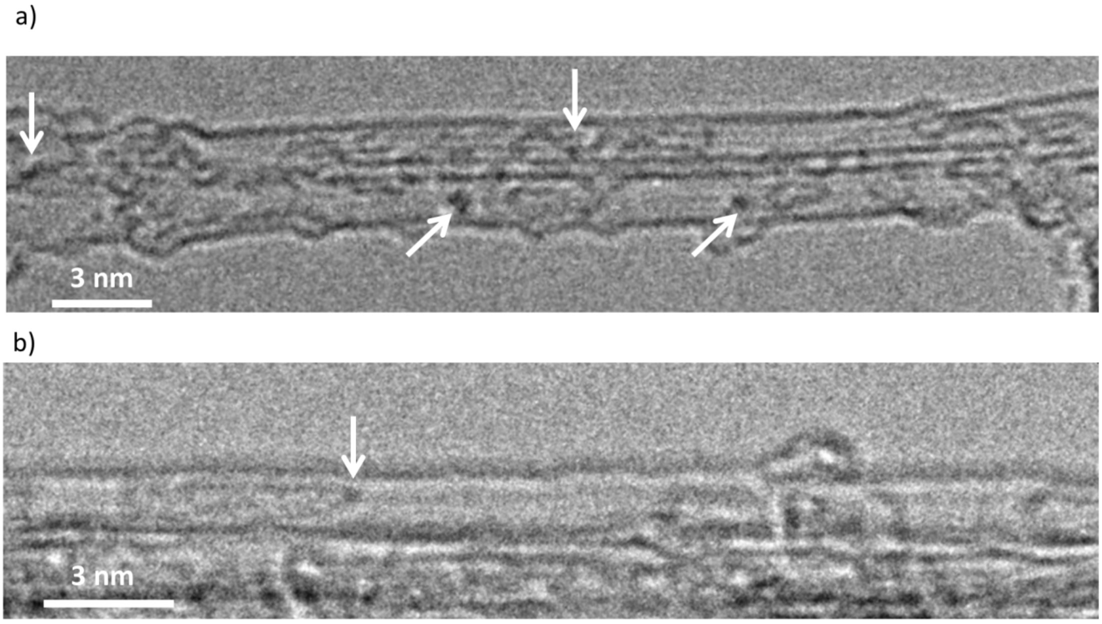

Figure S9. HRTEM images of $Cp^{Me}Mn(CO)_3$@SWNT showing Mn metal as dark contrast (white arrows) located solely inside the SWNT a) shows nanotube 1 (top) and 2 (bottom). b) shows nanotube 3. The number of metal atom is approximated to be 35 per nanoparticle.

Table 5. Calculation performed to determine the filling percentage of $Cp^{Me}Mn(CO)_3$@SWNT using TEM extrapolation approximations.

Nanotube	**1**	**2**	**3**
Length (nm)	32.9	32.9	27.7
Number of nanoparticles	2	2	2
Atoms per nanoparticle	35	35	35
Atoms per length nanotube in model (np nm^{-1})	2.77	2.77	2.77
Atoms per length nanotube in TEM experiment (np nm^{-1})	1.82	1.82	2.89
Filling percentage	**76 %**	**76 %**	**91 %**

S1.5.7 Summary

Table 6. A summary of all methods and the respective filling percentage.

Method	**Experiment number**	**Filling percentage (%)**
Chronocoulometry	1	84.45
	2	70.46
Nanotube weight difference	1	63
	2	62
	3	72
TGA	1	53.47
	2	47.61
	3	44.72
Quantitative EDX	1	12.5
TEM extrapolation	1	77
	2	77
	3	91

The filling percent ranges from 12.2 % to 91 %. As discussed we can assume that quantitative EDX yields a far lower than expected filling percentage. An average of the remaining methods presents an average filling percentage of 62 %. Through the application of a multitude of methods an approximate filling has been determined. Many approximations have been made but most of the methods are in agreement.

S2 Experimental

S2.1 Experimental methods

Chemicals and solvents were purchased from Aldrich and were used without further purification. SWNTs (P2-SWNTs, Carbon Solutions Inc., USA) were annealed in air at 600 °C for 20 minutes to open the end caps and remove amorphous carbon from the internal channel prior to use. Infrared spectroscopy was performed on a Bruker Tensor 27 spectrometer with 64 scans over a range of 1800 – 2100 cm^{-1} with 1 cm^{-1} resolution using the a sample pressed into a KBr pellet. KBr pellets were prepared using 0.1 mg of $Cp^{Me}Mn(CO)_3$@SWNT composite or $Cp^{Me}Mn(CO)_3$ and 300 mg of KBr. The press was evacuated on a vacuum line then pressed at 10 tonnes for 10 minutes. Electrodes were purchased from IJCambria and Metrohm. Electrochemistry experiments were performed on an Autolab PGSTAT302N potentiostat. TGA was performed on a TGA Q 500.

S2.1.1 Encapsulation of $Cp^{Me}Mn(CO)_3$ into SWNTs

Under an atmosphere of argon, freshly annealed SWNTs were dropped onto stirring $Cp^{Me}Mn(CO)_3$. The mixture was extensively sonicated then left to stir for 3 hours. The excess $Cp^{Me}Mn(CO)_3$ was removed by filtration on a PTFE membrane (pore size = 2 μm). Any remaining external $Cp^{Me}Mn(CO)_3$ was removed under a flow of nitrogen (24 hr).

S2.1.2 Electrode casting

The nanotube composite (0.5 mg) was sonicated (15 mins) in dry DMF (0.5 mL) to form an ink. 10 μL of the ink was cast onto the GCE and allowed to dry for 1 hour. The electrode was then rinsed in dry acetonitrile and allowed to dry.

S2.1.3 High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM analysis was performed on a JEOL JEM-2100F FEG microscope with an information limit of 0.12 nm at 100 kV. The imaging conditions were carefully tuned by lowering the accelerating voltage of the microscope to 100 kV and reducing the beam current density to a minimum. Suspensions of $Cp^{Me}Mn(CO)_3$ in HPLC grade isopropanol were dropped onto lacey carbon grids for TEM analysis.

S2.1.4 Energy Dispersive X-ray Spectroscopy (EDX)

Local EDX spectra were acquired for samples mounted on TEM grids using an Oxford Instruments INCA X-ray microanalysis system. The electron beam was condensed onto areas of specimens (bulk specimen or nanotube bundles) suspended over holes of the amorphous carbon film.