Supporting Information

Controlled covalent binding of antiferromagnetic tetramanganese complexes to carbon nanotubes

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In Figure S1, we show the STEM HAADF image of an unoxidized sample and the EELS data taken at different sites of the image. Spectrum 3 (blue) corresponds to the pure background, while spectrum 2 (green) contains a carbon and an oxygen signal from the bundle of carbon nanotubes. It shows that also pristine CNTs can possess defects that in principle can be functionalized. Therefore, few bright spots are found in this sample that also possess a manganese signal from attached molecules.



Figure S1. HAADF image (left) with corresponding EELS measurements (right) of a sample that was not oxidized but otherwise underwent the same procedure as the functionalized samples.

Since TEM is a very local method, we present here several more HAADF images (Figure S2 A-D) taken on the sample that was oxidized for 2 minutes. Though the contrast is not normalized between different images, it is clear that the coverage of the tubes is stronger compared to the unoxidized sample but less dense compared to the sample with an oxidation time of 30 minutes (Figure 3c).





The only heavy element present in the sample with $t_{ox} = 30$ min that can cause the scattering in HAADF mode after functionalization is indeed Mn as shown by an EDX spectrum of this sample (Figure S3) taken in bright field. Silicon and nitrogen peaks are due to electrons scattered from the silicon nitride membrane. Expected peak positions of Al, Mo, and Fe are indicated. No significant contributions of these elements are found. The scattering intensity in HAADF is proportional to Z^2 , with Z the atomic number. Thus, the contribution of Al to the intensity would be low, even if a signal were hidden in the background noise.



Figure S3. EDX spectrum of the sample oxidized in air for 30 minutes. The vertical scale is chosen such that small peaks are well visible. Therefore, the carbon signal is cut-off. Positions of C-K α , N-K α , O-K α , Al-K α , Si-K α , Mo-L α , Mn-K α , and Fe-K α peaks are indicated.