



Hard X-ray emission spectroscopy of transition metal complex 1-D arrays for nanomagnetic applications

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CH2862

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Report: Cobalt phthalocyanine (CoPc) and Nickel dimethylglyoxime (Ni(Hdmg)₂) were investigated as carbon nanotube encapsulated species (CoPc@CNT and Ni(Hdmg)₂@CNT) at ID26 using high-energy-resolution fluorescence-detected (HERFD) absorption spectroscopy, X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering in the valence band region (VB-RIXS). These systems have potential nanomagnetic applications due to unpaired electrons aligning along the NT length. We aimed to understand the electronic structure of Co and Ni in the molecular and encapsulated molecular forms to see if 1) any magnetic information can be obtained to understand the effect of linear encapsulation and 2) we can understand the changes in electronic structure due to encapsulation.

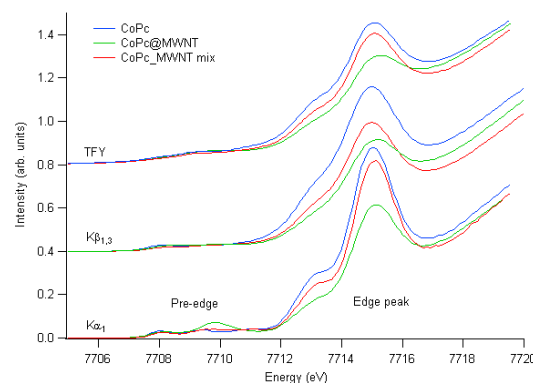
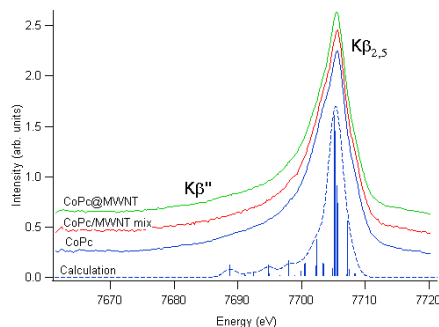
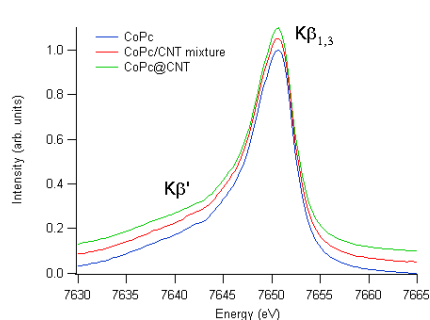


Figure 1: Left - $K\beta$ main line. Centre - $K\beta$ satellite line. The spectra show no differences between CoPc and CoPc@CNT. The DFT calculated $K\beta$ satellite line is shown for CoPc with peak components.

Figure 2: Total Fluorescence Yield (TFY) and HERFD-XAS spectra over the pre-edge and edge regions using the $K\alpha_1$ and $K\beta_{1,3}$ lines.

Results: CoPc@CNT

Figure 1 shows the $K\beta$ XES main and satellite lines for CoPc, a CoPc/CNT mixture and CoPc@CNT. There are no differences seen between the samples, suggesting that encapsulation in CNTs does not affect the spin enough to be detected using $K\beta_{1,3}$ XES. DFT calculations in ORCA [1] show extensive orbital delocalisation across the Pc molecule which prevents any 'pure' metal-ligand MOs existing, thus any $K\beta''$ peaks forming and any differences being seen between the different samples.

The HERFD spectra (seen most easily using the $K\alpha_1$ line) have different pre-edges, which arise from Co $1s-3d$ transitions. The large rising edge peak is due to $1s-4p_z$ transitions. It is of lower intensity and is at higher energy in CoPc@CNT than CoPc, suggesting a more oxidised Co atom in the encapsulated CoPc, due to electron donation from the molecule to the nanotube. DFT calculations suggest that symmetry breaking upon encapsulation, from D_{4h} to C_{4v} , allows different orbital mixing to take place. This increase in $p-d$ hybridisation splits and lowers the intensity of the edge peak while increasing the pre-edge peak intensity.

Results: Ni(Hdmg)₂@CNT

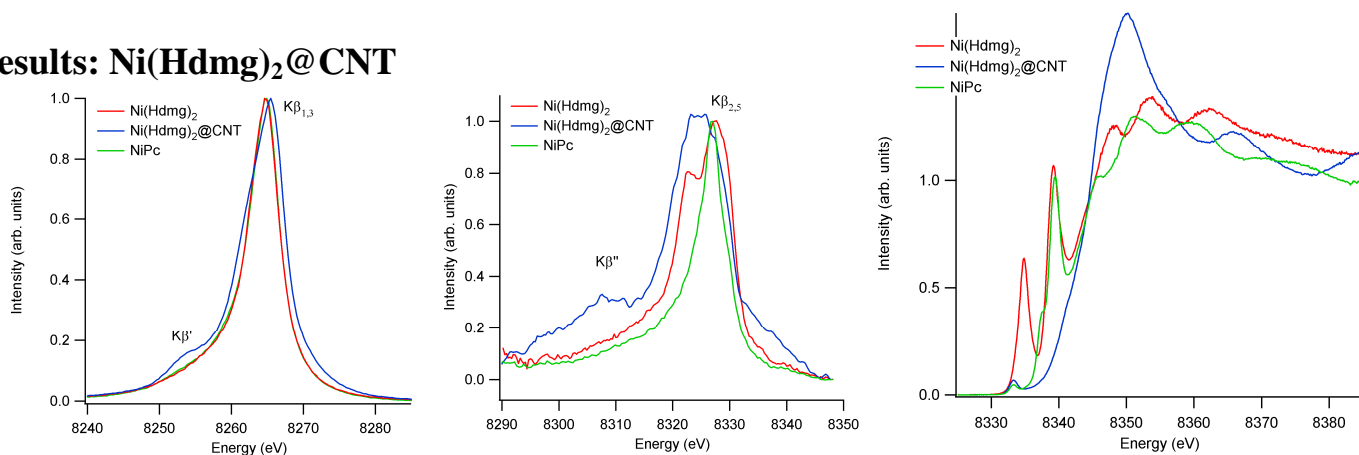


Figure 3: Left – $K\beta$ main line. Centre – $K\beta$ XES satellite lines. Right – HERFD. The spectra differ between Ni(Hdmg)₂ and Ni(Hdmg)₂@CNT. The Ni(Hdmg)₂@CNT data resemble spectra expected for an oxide. NiPc is shown for comparison

In Figure 3, the $K\beta$ main lines show Ni(Hdmg)₂@CNT has higher spin than Ni(Hdmg)₂ from the presence of a $K\beta'$ peak. The $K\beta$ satellite line for Ni(Hdmg)₂@CNT resembles that of an oxide. Early DFT models of NiPc and Ni(Hdmg) agree well with the measured data and further analysis is planned. No $K\beta''$ peaks are seen for Ni(Hdmg)₂ or NiPc due to MO hybridisation over the entire molecule, as with CoPc. The Ni(Hdmg)₂ HERFD spectrum shows a very strong pre-edge from $1s$ - $3d$ transitions and an edge peak from $1s$ - $4p_z$ similar to NiPc. Again the HERFD spectrum of Ni(Hdmg)₂@CNT looks like an oxide of Ni. This suggests the molecule is converted to a different species upon encapsulation.

VB RIXS spectra

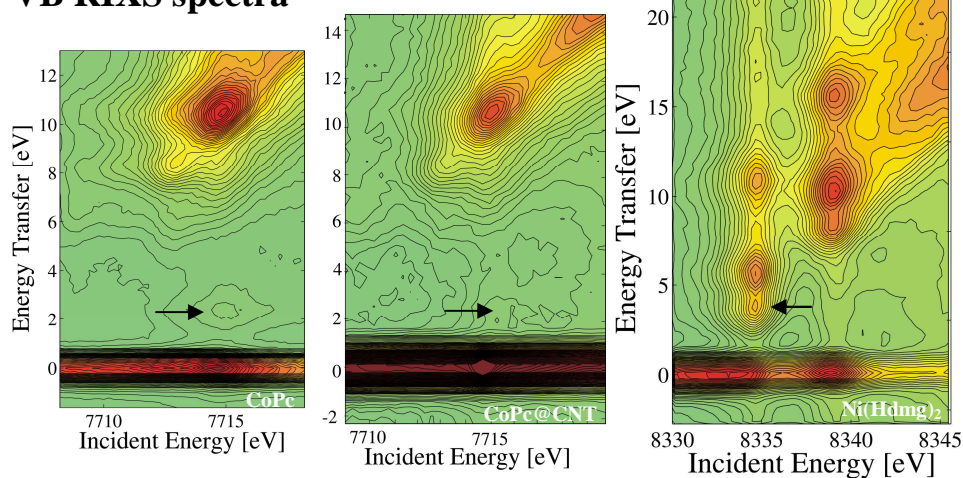


Figure 4: VB RIXS planes taken over the $K\beta_{2,5}$ line and metal K edge. The electronic structure of the molecules is mapped out close to the Fermi level (Elastic peak at 0eV energy transfer, low energy transfer peaks shown with an arrow)

The VB RIXS planes in Figure 4 show the electronic transitions close to the Fermi energy. There is a low energy peak in CoPc (and in CoPc@CNT but less clear) at 2.4eV energy transfer. The VB RIXS plane of Ni(Hdmg)₂ shows many transitions including low energy transfer peaks at 3.7eV. These suggest d - d^* excitations [1]. We plan to calculate these plots using ORCA, a DFT code in development for calculating RIXS. UV-Vis data will also be taken to try and match up the low energy transfer transitions.

Conclusions and further work

Spectral changes are seen in Ni(Hdmg)₂ upon encapsulation which are not observed for CoPc, namely a change in spin state and conversion to an oxide-type material. The molecular geometry of CoPc is found to remain intact but change slightly upon encapsulation to a reduced symmetry, as shown in DFT calculations. For Ni(Hdmg)₂ however, structural changes upon CNT encapsulation cause the large differences in electronic structure. The changes may also be due to a reaction occurring inside the CNT for Ni(Hdmg)₂. The RIXS data will be consolidated with DFT calculations using the ORCA code, and with UV-visible measurements to understand the low energy transfer excitations. Comparisons to oxide reference materials may be measured for Ni(Hdmg)₂.

References:[1] ORCA DFT code by F. Neese *et al.*, University of Bonn, [2] Schulte, K. *et al.*, (2007), *Adv. Mat.*, **19** (20) 3312-3316, [3] Schulte, K. *et al.*, (2008), *J. Phys.: Conf. Series*, (IVC17/ICSS13/ICN+T2007), **100**, 012017, [4] Hatsui, T. *et al.*, (1998), *J. Elec. Spec. Rel. Phenom.*, **88-91** 405 – 409