

Molecular Encoding at the Nanoscale: From Complex Cubes To Bimetallic Oxides[\*\*]

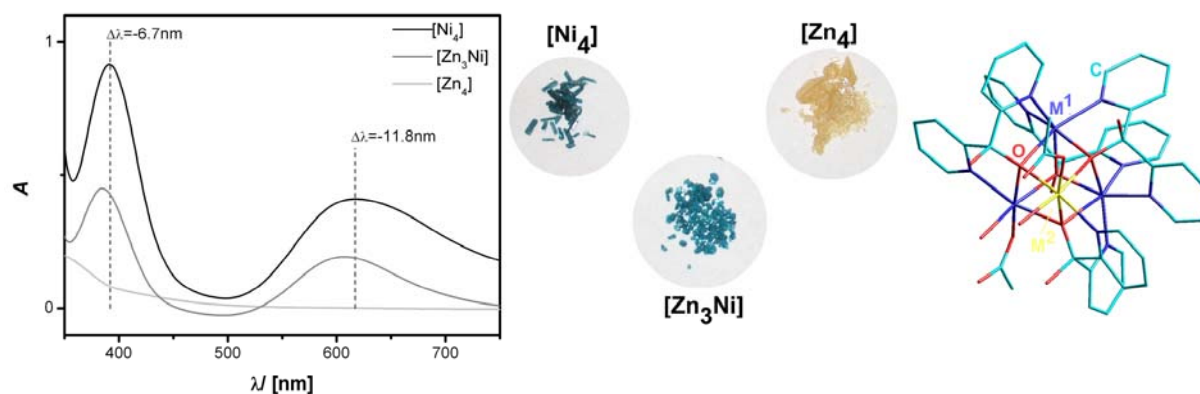
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**SII EXPERIMENTAL:** All chemicals were received from Aldrich and used without further purification. The preparation method for the clusters were adapted from the literature where the synthesis of the monometallic is reported.<sup>[22]</sup> Here, different ratios of metal acetates were applied in the synthesis mixture.

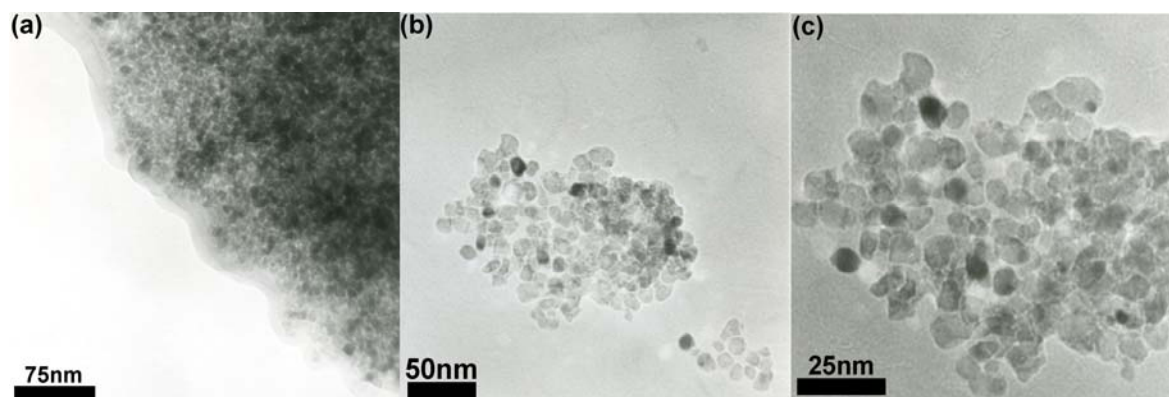
TGA was performed by an equipment by Rubotherm using a magnetic coupling balance. X-ray diffraction (PXRD) analyses of all powder samples and deposited particles were performed on a Bruker - AXS D8 Advance using  $\text{Cu}_{K\alpha}$  - radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a position-sensitive-detector (PSD). Conventional transmission electron microscopy (TEM) was performed on a Philips CM12 microscope (LaB<sub>6</sub> filament, 120 kV, Twin lens) equipped with an energy dispersive X-ray spectrometer (EDX, type Oxford Link). The powder samples obtained by solid-state decomposition were suspended in cyclohexane using an ultrasonic bath for 5 min and then left to dry on a carbon-coated TEM grid. UV/Vis spectra were recorded using a Perkin Elmer Lambda 20 spectrometer equipped with a reflecting sphere, Labsphere RSA-PE-20. ESI-MS spectra were recorded using a BRUKER Acquire mass spectrometer.

## SI2 Optical properties of mixed clusters and structure:

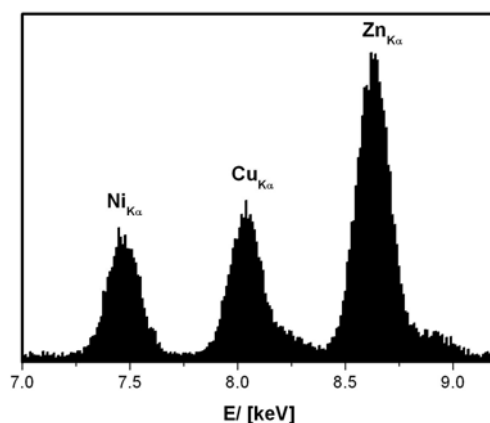


All heterocubane precursors can be obtained in single-crystalline form. The colour of the bimetallic compounds  $[M^1_{4-y}M^2_y]$  (light blue for  $[Zn_3Ni]$ ) is not a simple superposition of the colour of the parent compounds (dark blue for  $[Ni_4]$  and colourless/ yellow for  $[Zn_4]$ ) but a characteristic shift of the absorption maxima occurs as indicated by UV/Vis spectroscopy (recorded in  $H_2O$ ). This confirms the findings from ESI-MS spectra that new mixed clusters are formed and not just simple mixtures of the parent compounds. However, despite the single-crystalline nature of the compounds it was not possible to securely assign the metal type to the molecular structure determined by single-crystal analysis. This is caused by a combination of factors: The difference in electron-density between  $Zn^{2+}$  and  $Ni^{2+}$  for instance is very small, while both ions are octahedrally coordinated in the clusters. Furthermore, the position of the second metal is highly disordered relative to the neighboring clusters in the crystal lattice. Furthermore, as the ESI-MS spectra of the compounds prove there is a high tendency for co-crystallisation independent from the molecular composition of the clusters. However, the introduction of the second metal seems to introduce asymmetry into the cluster framework. Although all metal centers are octahedrally coordinated it is seen that two metal ions are coordinated only by one pyridine unit (with water as an additional ligand) and two are coordinated by three pyridine units, while in the single-metal clusters every metal center is equally coordinated by two pyridines from the (dpd-H)-ligand.

## SI2: TEM and EDX:

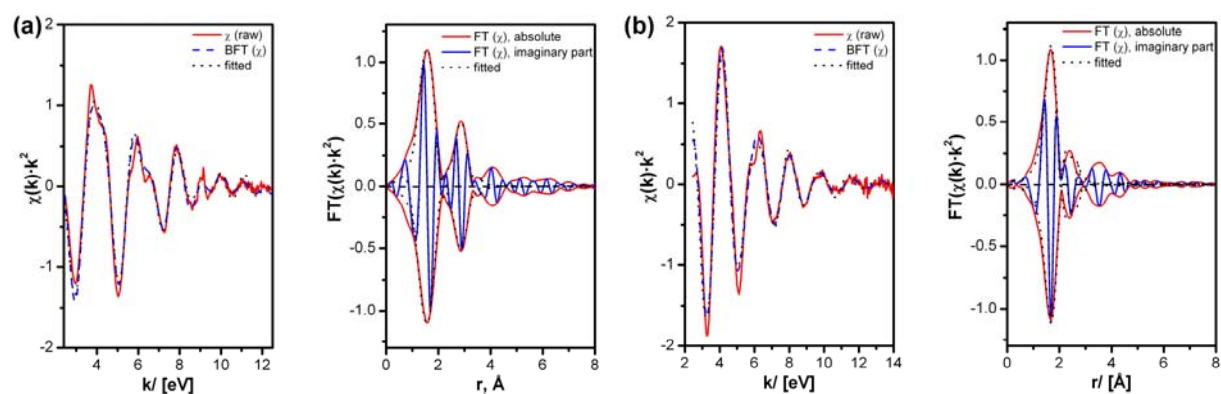


The size of the nanoscaled particles obtained from  $[\text{Zn}_3\text{Ni}]$  for  $T_d = 250^\circ\text{C}$  correlates well to the PXRD-data. Initially, the particles inside large agglomerates seem to be covered by a thin shell of lower electron contrast which is presumably organic in nature (see image a). EDX spectra indicates the the ration of Zn to Ni in these particles is of the order of 73% to 27%, thus, in correlation to the expected 3:1 stoichiometry.



However, the single particles are highly agglomerated at this stage. This made it impossible to perform the EDX on one single particle. One also has to realized that the electron beam we used for determination of EDX is quite large. To study one particle was, thus, not possible. However, by applying a washing routine using acetone, it was possible to remove most of the organics from the materials. As a result, smaller agglomerates could now be obtained (see image (b and c)). The size of the single oxidic particles is now visible much better, and it can be shown that the particle size from TEM (10-11nm) is very close to the particle size from XRD (10nm). Furthermore, the agglomerates seem to contain only crystalline particles.

### SI3 XAS-Modelling



(a) shows the Zn-K-edge XAS data and a fit assuming a wurtzite type ZnO-lattice with 1/3 of the cations replaced by  $\text{Ni}^{2+}$ . A fit based on a pure Zn containing ZnO lattice was also performed (not shown) but gave worse agreement. (b) shows the Ni-K-edge XAS data and the fit for the mentioned structure.