



Understanding the electronic structure of titanium complexes using RIXS and UV-visible spectroscopy on ID26



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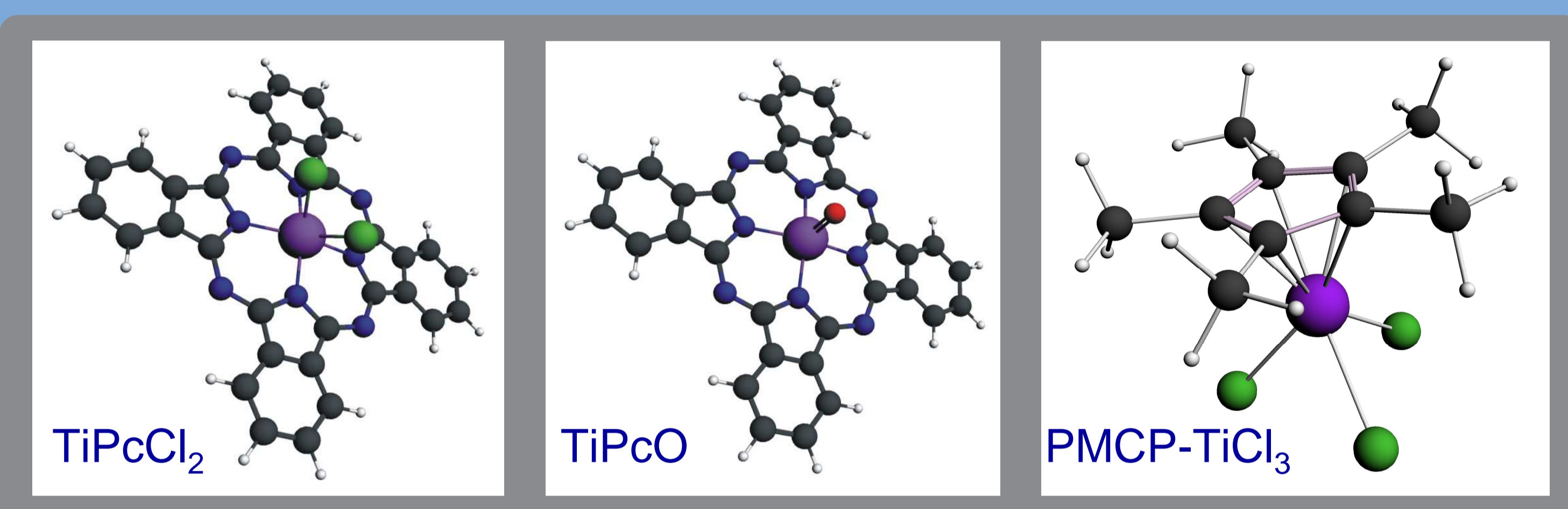
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The aim of this research is to understand the electronic structure in metal (titanium) complexes using K-edge XANES, non-resonant and resonant XES spectroscopy, and UV-visible spectroscopy.

We discuss the relative advantages and disadvantages of these different techniques, and show comparisons between the different spectra recorded.

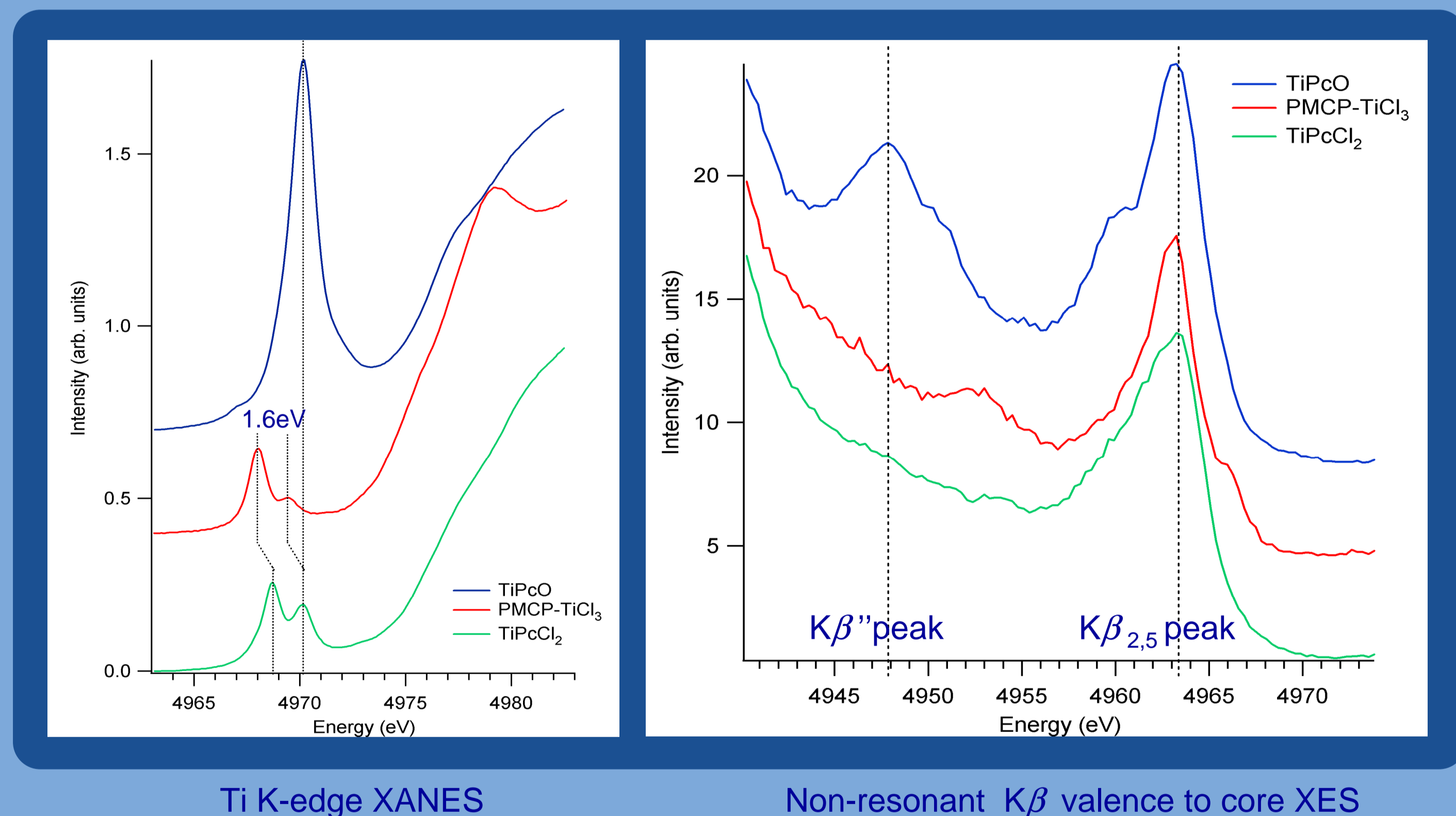
Ti phthalocyanines (TiPc)

TiPcO is a common choice for IR sensitised devices, and is used in molecular solar cell development. Understanding the electronic structure of TiPcO and related compounds is therefore crucial to future developments. Powder samples of TiPcO, and the related molecule TiPcCl₂ were studied. PMCP-TiCl₃ was included as a model Ti-Cl system.



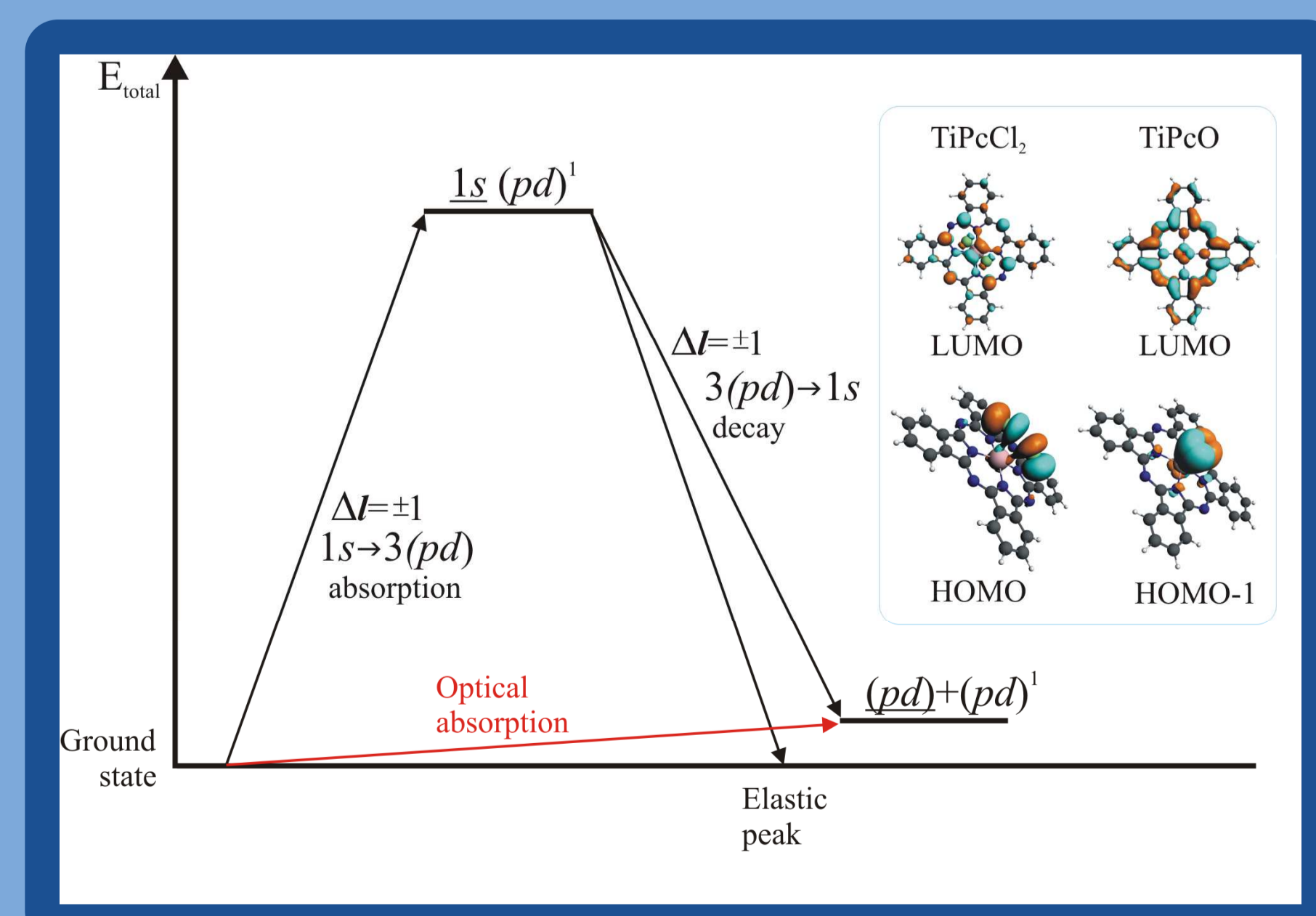
Non-resonant XANES and XES spectra

K-edge XANES records information about the crystal field splitting and atomic symmetry in the pre-edge region. Valence to core XES probes the effect of the ligands on the metal electronic structure. Both measurements involve an ionised species with a hole in the valence band and are element specific.



Total energy diagram

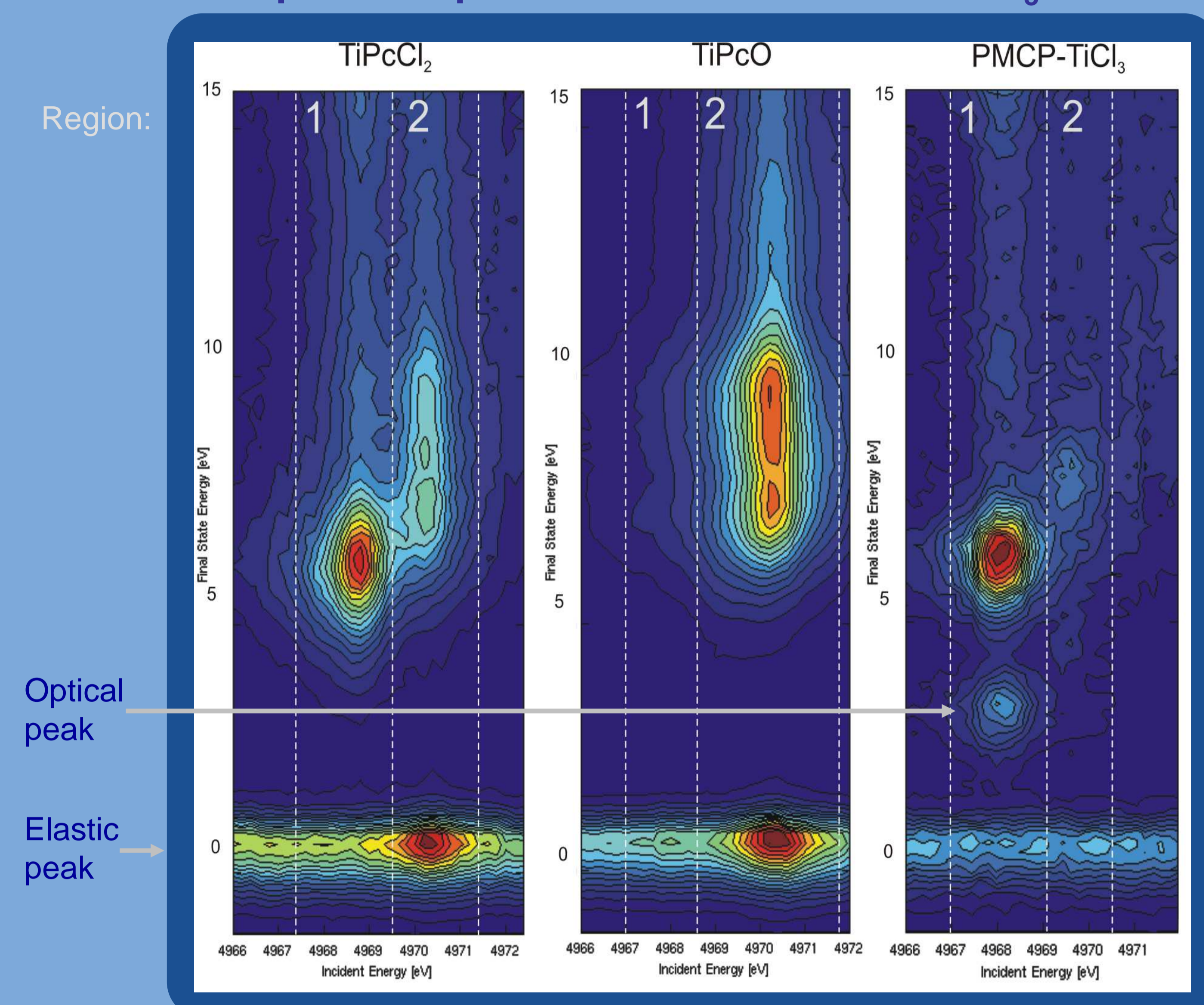
The energy diagram below shows the optical transition accessed through RIXS (black) and in UV-visible spectroscopy (red).



The electrons in RIXS are excited into the *pd* molecular orbitals (MOs). The pre-edge is found to be mostly Ti *p*-like from DFT calculations. There is some Ti *d*-like contributions also, due to the low symmetry of the molecules.

After excitation, an electron relaxes from another *pd* MO to fill the 1*s* core hole resulting overall in an optical range transition, detected in RIXS and UV-visible spectra.

2-D RIXS maps with optical features for PMCP-TiCl₃

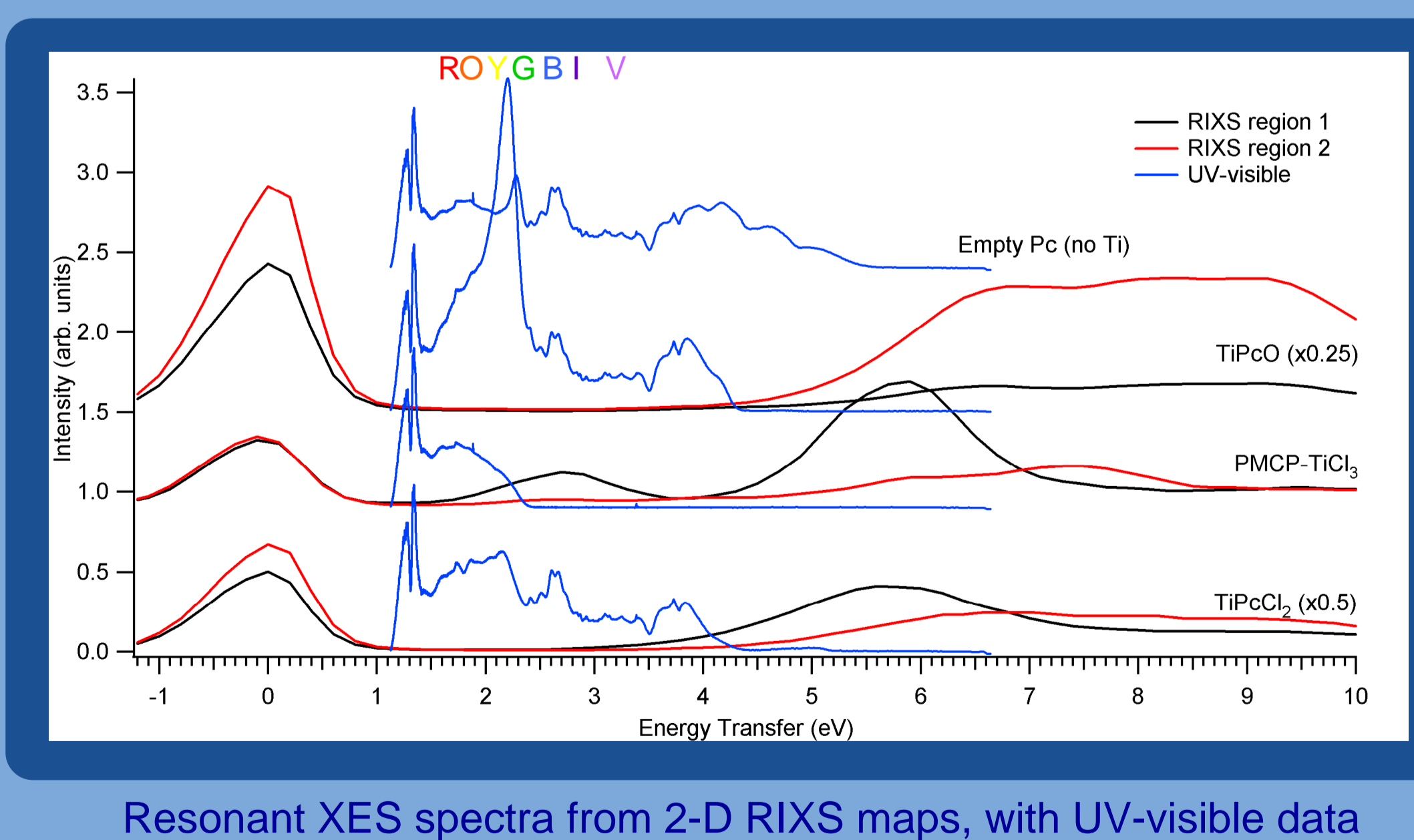


RIXS maps were measured using the $K\beta_{2,5}$ emission line over the Ti K edge. RIXS is element specific, unlike UV-visible, so we can attribute transitions directly to the metal atom being probed. Also, some forbidden optical transitions (*d-d* excitations) can be accessed in RIXS as there are different selection rules.

Note the optical peak at 2.7eV for PMCP-TiCl₃ and the elastic peak enhancements in the Pc molecules. TiPcO does not have a pre-edge peak in region 1.

UV-visible spectra

Unlike RIXS, UV-visible spectra are influenced less by momentum transfer, and the spectra have a much higher energy resolution although they have a shorter energy range.



The samples were suspensions (TiPcO and TiPcCl₂) and a solution (PMCP-TiCl₃) in ethanol.

There is no obvious correlation between the two data sets, which may be due to different selection rules and momentum transfer in the two techniques.

Conclusions

- UV-visible and RIXS spectra provide complementary information the electronic structure of metalloorganic systems.
- The challenge is to interpret these measurements to determine the electronic structure of these interesting materials.

References:

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3. P. Glatzel and U. Bergmann, "High resolution 1*s* core hole spectroscopy in 3*d* transition metal complexes—electronic and structural information", *Coord Chem Rev*, 249(1-2), 2005, pp65