With the advance of nanotechnology, a wide variety of hybrid organic-inorganic interfaces have been extensively investigated for their important role in molecular electronic and spintronic devices. The understanding of the structural, electronic and magnetic properties of these interfaces represents a fundamental step for an effective tailoring and optimization of potentially novel devices. To this aim, I will show how a surface-science approach based on synchrotron-based techniques and scanning probe microscopies is a suitable solution for describing model systems in which different properties can combine increasing the interface complexity. In this perspective, I will report on (i) semiconductor molecules at the interface with the technologically relevant TiO2(110) surface and (ii) metal coordination compounds, i.e. Single Molecules Magnets (SMMs), on metallic and insulating substrates. In both cases STM, photoelectron (XPS and UPS) and adsorption spectroscopies (XAS) have been used to get access to the structural and electronic properties of the hybrid system. Other aspects, such as the charge transfer occurring between the TiO2 and semiconductor molecules, have been investigated by means of Resonant Photoemission Spectroscopy. In the case of SMMs, low temperature X-ray Magnetic Circular Dichroism measurements have been used to probe the surface-mediated molecular magnetism.