

# On Surface trans-metalation of Zinc Tetraphenyl Porphyrin on rTiO<sub>2</sub>(110)

Luca Schio<sup>1</sup>, Massimo Tormen<sup>1</sup>, Gregor Bavdek<sup>2</sup>, Luca Floreano<sup>1</sup>

<sup>1</sup>CNR-IOM, Laboratorio TASC, Basovizza S.S. 14, m 163.5, I-34149 Trieste (Italy)

<sup>2</sup>Faculty of Education, University of Ljubljana, Kardeljeva ploscad 16, SI-1000 Ljubljana (Slovenia)

Metalloporphyrins and Titanium Dioxide, TiO<sub>2</sub>, are both promising candidates for photovoltaic and photocatalysis applications. The electronic properties of porphyrins can be tuned by the proper choice of the central metal ion, as well as by varying the macrocycle substituents [1]. TiO<sub>2</sub> shows interesting physicochemical properties [2], which enables it to work as a multifunction material, from sunscreens to photovoltaic cells. Among the different TiO<sub>2</sub> polymorphs, the (110) surface of the rutile crystal, rTiO<sub>2</sub> (110), is the most common and easily produced. It is thus not surprising that the interface between porphyrins and rTiO<sub>2</sub> has been extensively studied [3], being possible the opening of a new scenario for electronic applications. In this perspective, the stability of such organic-inorganic interface must be investigated. In the presented work, the reactivity of Zinc Tetraphenyl Porphyrin (ZnTPP) on rTiO<sub>2</sub>, as a function of temperature and coverage, was studied by means of X-ray Photoelectron Spectroscopy (XPS), Near-edge X-ray Absorption Spectroscopy (NEXAFS) and Scanning Tunneling Microscopy (STM). The spectroscopic results (shown in fig.1) show a dramatic change in the molecule core levels upon thermal treatment: although Zinc is gradually lost up to 400°C, the single peak in the N 1s XPS clearly indicates the presence of a fully coordinated macrocyclic ring, suggesting a trans-metalation reaction of the ZnTPP with a Ti atom from the substrate.

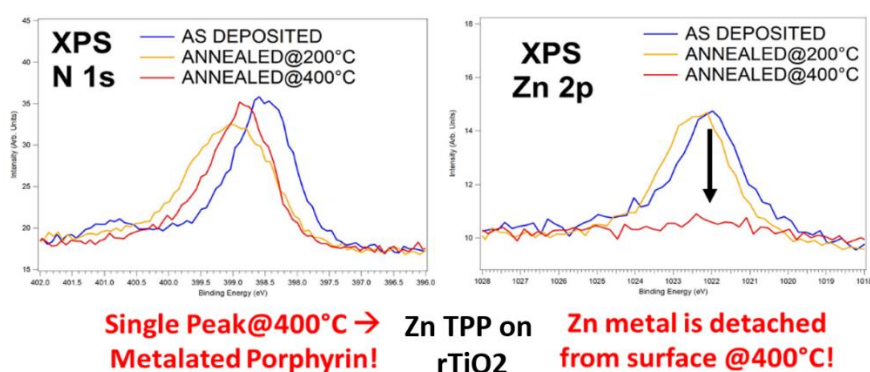


Fig. 1. XPS Spectra at the Zn 2p and N 1s edges of ZnTPP on rTiO<sub>2</sub> as a function of temperature.

## References:

- [1] J. M. Gottfried, Surf. Sci. Rep. 70, 259-379 (2015).
- [2] U. Diebold, Surf. Sci. Rep. 48, 53 (2003); A. Fujishima et al., Surf. Sci. Rep. 63, 515 (2008).
- [3] M. K. Kremer et al., Appl. Surf. Sci. 564, 150403 (2021); G. Lovat et al., J. Phys. Chem. C 121, 13738 (2017); G. Lovat et al., Phys. Chem. Chem. Phys. 17, 30119 (2015) and references therein.