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Spectroscopic investigations of nitroxide persistent organic radicals. Future perspectives in view of Elettra 2.0: the MOST beamline

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Nitroxide free radicals (NRs), such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, Fig.1a), are organic radicals stabilized by the delocalization of their unpaired electron between N and O atoms as well as by screening of the paramagnetic center by bulky substituents [1]. They are employed in catalysis [2] and, in chemical synthesis, as initiators in radical-chain polymerization and redox reactions [3]. Moreover, the magnetic moment of their unpaired electrons makes them suitable for quantum computing, spintronics and molecular magnetism [4].

We will show the synchrotron radiation investigations performed on TEMPO and three of its analogues, i.e., Di-tert-butyl nitroxide (DTBN), nit8 and nit9 (Fig.1) in gas phase and as thin films, with the support of Density Functional Theory (DFT) calculations. In gas phase [5], we exploited X-ray Absorption Spectroscopy (XAS) and Resonant Photoemission Spectroscopy (ResPES), to determine N and O atomic contributions to the resonant valence band structures. This elucidated the role of the Single Occupied Molecular Orbital in the photoexcited molecules. Afterwards, we grew molecular films of TEMPO and nit9 on Au(111) and Cu(111) in ultra-high vacuum (UHV) and we performed X-ray Photoemission Spectroscopy (XPS) and XAS. To the best of our knowledge, this was the first time NRs molecular films were achieved under well-controlled UHV conditions. In the films the molecular properties are preserved on Au(111) and consistently modified on Cu(111). Moreover, while the amide functional group is not influencing the behavior of the isolated photoexcited molecules in gas phase, it plays a fundamental role in the molecular films. Indeed, its presence can prevent NRs undergoing a complete decomposition of the nitroxide paramagnetic center upon adsorption on the more reactive Cu surface.

The obtained results mark a step forward towards the full comprehension not only of through-bond effects in the isolated molecules but also of the through-space effects in the adsorbate systems and are an important proof of principle in view of the realization of organic radical-based devices.

In the end, we would like to spend few words about the conceptual design of MOST (Molecular and Optical Science Technology), the new beamline of Elettra 2.0, replacing the existing GasPhase and Circular Polarization (CiPo) beamlines. MOST innovative optical layout will employ state-of-the-art technologies, to allow a full exploitation of the improved performances of Elettra 2.0. The higher flux of the new source will permit the spectroscopic characterization of a large variety of highly reactive gaseous species, up to now hampered by the low density of the target. Together with the implementation of a more performing electron analyzer, it will help, for example, the realization of ResPES experiments on the most common C, N and O K-edges, affected by a poor statistics and a low count rate on the current beamlines.

[1] J. H. Osiecki, E. F. Ullman J. Am. Chem. Soc., 1968, 90 (4), 1078.

[2] Z. Ma, K. T. Mahmudov, V. A. Aliyeva, A. V. Gurbanov, A. J. L. Pombeiro Coord. Chem. Rev., 2020, 423, 213482.

[3] K. Zhang, M. J. Monteiro, Z. Jia, Polym. Chem., 2016, 7, 5589.

[4] Y. Borozdina, E. Mostovich, V. Enkelmann, B. Wolf, P. T. Cong, U. Tutsch, M. Lang and M. Baumgarten J. Mater. Chem. C, 2014, 2, 6618.

[5] R. Totani, I. Ljubić, A. Ciavardini, C. Grazioli, F. Galdenzi, M. de Simone, M. Coreno Phys. Chem. Chem. Phys. 2022, 24, 1993.

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