Reversible Radical Formation of Naphthalene Diimide Adsorbed on KCl in the Monolayer Regime.

E. Momo,[1] E. Geagea,[1,2] S. Clair,[1] L. Giovanelli,[1] L. Nony,[1] O. Pilone, S. Bertaina,[1] V. Dolocan,[1] A. Savoyant,[1] F. Cherioux,[3] V. Luzet,[3] A. Rochefort,[4] C. Loppacher [1].

[1] *Aix Marseille Université, CNRS, Université de Toulon, IM2NP, Marseille, France*
[2] *Department of Physics, University of Basel, CH-4056 Basel, Switzerland*
[3] *Université Marie et Louis Pasteur, CNRS, FEMTO-ST, Besançon, France*
[4] *Département de génie physique, Polytechnique Montréal, Montréal (Québec), Canada*

Aromatic diimide moieties have been reported to undergo electrochemical reduction (in solution) to form relatively stable radical anions (1). Besides electrochemical reduction, diimides also show photochemical reduction, particularly a photoinduced intramolecular electron transfer (PIET) has been observed for naphthalene diimides in the form of powder and crystals (2).

In this work, we present the deposition of naphthalene diimides consisting of two donors and one acceptor (the diimide) group on bulk and thin films of KCl under ultrahigh-vacuum conditions. Combined ncAFM and STM measurements show that the molecules form a highly ordered monolayer with planarly adsorbed molecules on KCl. Differential Reflectance Spectroscopy (DRS reflects the optical absorption spectra) during the deposition of the organic layer confirms the formation of a radical species upon illumination. The radical is stable over hours and can be reversibly excited after relaxation.

These results are compared with DFT calculations, EPR (Electron Paramagnetic Resonance) spectra of thin films and powder, and UV-vis spectroscopy in solution to understand the formation of the radical and its magnetic and optical properties. These results indicate the potential use of these molecules as organic Spin-State Photoswitches.

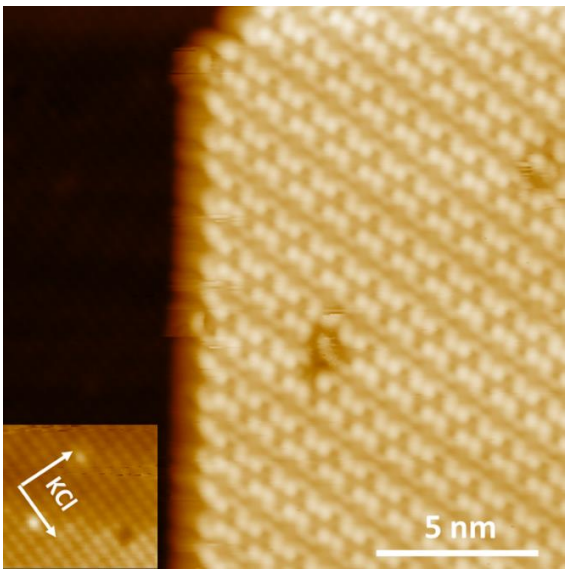


Figure : *Topography image (STM) of a monolayer of naphthalene diimide adsorbed on a thin film of KCl on Au(111). Lower left part, contrast highlighted to show the KCl substrate periodicity. A point-on-point epitaxy of planarly adsorbed molecules is observed.*

REFERENCES

1. A. Viehbeck et al., *J. Electrochem. Soc.*, **137**, 1460 (1990); S.K. Lee et al., *J. Am. Chem. Soc.,* **121**, 3513 (1999).
2. Y. Matsunaga et al., *Chem. Eur. J.*, **20**, 7309 (2014).