Oral presentation

Nitro-to-*endo*-nitrito isomerization in the solid state: unravelling light-induced mechanism of the process

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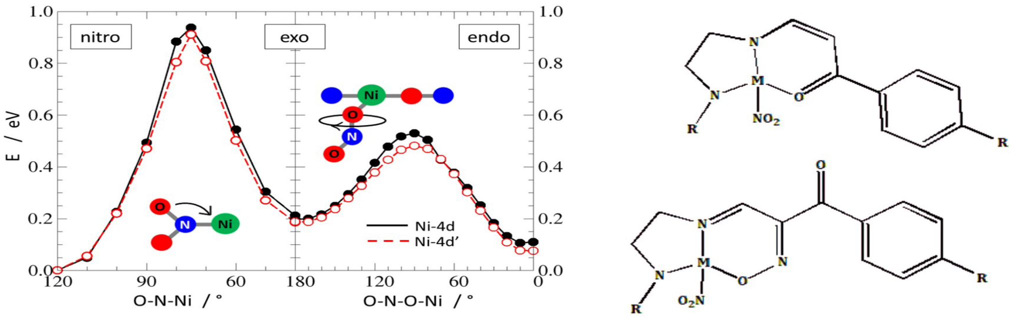
Molecular switches are systems that undergo chemical transformations under the influence of an external stimuli, such as temperature changes, irradiation, or electric field. Changes in molecular structure may be accompanied with alterations in physical properties, making them promising materials for various applications e.g. in materials science [1], optoelectronics [2] and medicine [3].

Transition metal complexes containing ambidentate ligands, such as –NO_2, -SO_2 or –NO, constitute an interesting group of molecular switches. These ligands exhibit multiple binding modes with the metal centre which can dynamically switch in response to an external stimuli. The -NO_2 group, presented in this project, adopts four linkage isomers in mono-nuclear complexes: nitro-(η^1-NO_2), *exo*-nitrito-(η^1-ONO), *endo*-nitrito-(η^1-ONO) and κ-nitrito-(η^2-O_2N) [4].

Depending on the central metal atom, supporting ligands and crystalline environment, linkage isomerisation can proceed in different ways. Understanding of the influence of these factors and, importantly, of the isomerization mechanism, is essential in designing novel efficient photoswitches for practical applications.

The presented project focuses on describing the reaction mechanism of the nitro-to-*endo*-nitrito isomerisation under light irradiation. The experiments were performed on a series of square-planar complexes, with N,N,O-chelating supporting ligands, containing single nitrite group in the molecule. The examined compounds are highly responsive to light irradiation in the 10 – 200 K temperature range. In order to trace the reaction path experimentally, techniques such as *photo*IR and *photo*XRD were used. It was observed that during light irradiation nitro binding mode converts to the *exo*-nitrito form which is transformed to the *endo*-nitrito isomer with further irradiation. This establishes the nitro $\rightleftarrows$ *exo*-nitrito $\rightleftarrows$ *endo*-nitrito reaction path as the most probable. The experimental findings were supported by theoretical calculations containing energy optimization, intermolecular interactions energy calculations and reaction path calculations.



(a) (b)

Figure 1. ***(a)*** theoretically modelled nitrio-to-*endo*-nitrito isomerisation reaction path calculated for selected compounds, ***(b)*** general structures of the studied systems.

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