Insight into trans-[Ru(NO)(py)4F](ClO4)2 photo-commutation properties by solid state NMR and DFT calculations

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Résumé

Photoinduced isomers can be generated in a variety of compounds, each having its specific structural response and wavelength sensitivity. This gives rise to interesting properties such as photochromism and photorefractivity for holographic data storage and optical switches. Fundamental questions in this context are to what extent the electron density distribution in the photo-generated isomer has changed with respect to the ground state configuration, as well as how the structural and electronic characteristics of the photoswitches are linked to the thermal stability and optical properties of the photoproducts. In this communicatioin we present solid-state NMR results obtained on the complex trans-[Ru(py)4(15NO) F](ClO4)2,.where the quasi-fourfold axis F-Ru-15N-O is nearly linear in the ground state and the unit cell contains two crystallographic independent molecular units. Upon irradiation, two metastable linkage isomers can be generated, one by rotating NO by about 90∘ (MS2) and one by an inversion of the NO ligand by 180∘ (MS1). We show here the successful low temperature trapping and SSNMR observation of the diamagnetic light induced metastable state MS1. In order to gain insight into the bonding properties and changes of the electron density upon photo-isomerization, we compare the 15N and 19F solid-state NMR results with those obtained from DFT calculations based on our recent X-ray diffraction measurements. Interestingly, we observe different commutation properties within the same crystal for the two inequivalent cations and supply an explanation based on local changes in electron density and orbital populations provided by the DFT calculations.

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