

## Extending the $^3\text{MLCT}$ excited-state lifetimes of Ni(II) complexes in solution

Tomohiro Ogawa, Narayan Sinha, Oliver S. Wenger

Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland

E-mail: tomohiro.ogawa@unibas.ch

Square planar Ni<sup>II</sup> complexes have received growing interest in the field of photoredox catalysis.[1] Although excited states of Ni<sup>II</sup> complexes seem to play important roles in photoredox catalytic reactions, investigations of electronically excited states and their relaxation pathways in Ni<sup>II</sup> complexes are yet scarce. In most of the so far reported square-planar Ni<sup>II</sup> complexes, initially formed metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) states decay very rapidly to energetically lower-lying metal-centered (MC) states.[2] Here, we present our attempts to extend the MLCT excited state lifetimes in solution at room temperature. Toward this goal, we employed a tridentate chelate ligand providing a rigid coordination geometry and a strong ligand field. To complete the square planar coordination geometry, sterically demanding (monodentate) isocyanides were used to further enhance structural rigidity and to protect Ni<sup>II</sup> from solvent coordination (Figure 1A inset).

Figure 1A presents the UV-Vis absorption spectra of the three synthesized Ni<sup>II</sup> complexes, showing relatively intense MLCT bands around 400 nm. After excitation into these MLCT bands, ground-state bleaching (GSB) of that band was observed and a characteristic excited-state absorption (ESA) feature appeared around 450-500 nm (Figure 1B). The decays of the ESA were substantially faster than the GSB recoveries, suggesting that the initially populated MLCT state with its diagnostic ESA signal between 450 and 500 nm decays to an energetically lower-lying MC state. The MLCT decays showed extended lifetimes upon increasing the steric demand of the monodentate isocyanide ligand.

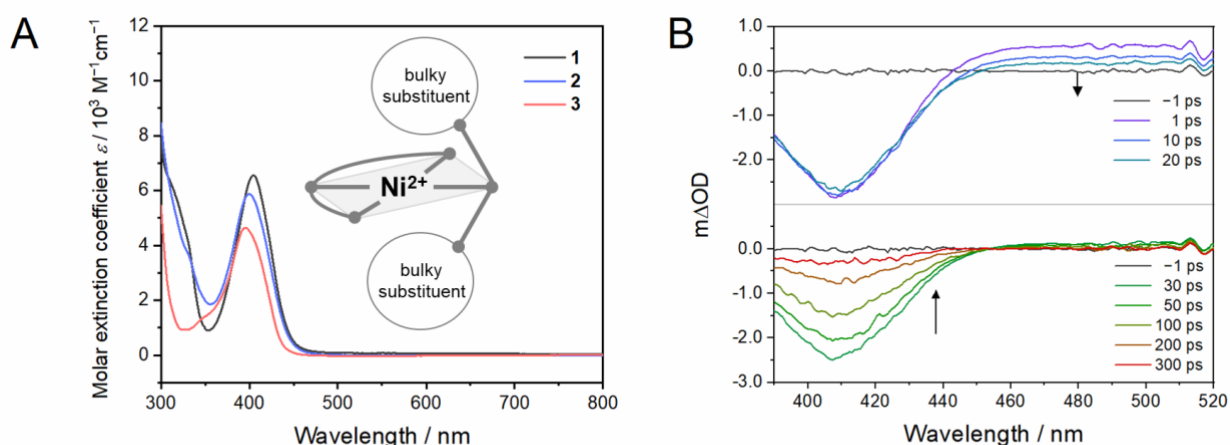


Figure 1. A) UV-Vis absorption spectra of Ni complexes in CH<sub>3</sub>CN at RT. B) Transient UV-vis absorption spectra

[1] Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; MacMillan, D. W., *Science* **2017**, 355, 380.

[2] Ting, S. I.; Garakyaraghi, S.; Taliaferro, C. M.; Shields, B. J.; Scholes, G. D.; Castellano, F. N.; Doyle, A. G., *J. Am. Chem. Soc.* **2020**, 142, 5800. Hong, J.; Fauvell, T. J.; Helweh, W.; Zhang, X.; Chen, L. X., *J. Photochem. Photobiol., A* **2019**, 372, 270