

Ultrafast Photochemical Dynamics of a Magnetically Bi-stable Azo-functionalized Ni-Porphyrin Spin Switch

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The azopyridine-functionalized Ni-porphyrin **1** (Figure 1) shows magnetic bi-stability in homogeneous solution at room temperature [1]. On irradiation at $\lambda \sim 435$ nm, the four-coordinate low-spin Ni complex switches to its high-spin state, which is trapped by axial coordination of the azopyridine ligand that undergoes simultaneous *trans*-to-*cis* isomerization. On irradiation at $\lambda \sim 500$ nm, this process is reversed and the low-spin state is efficiently recovered.

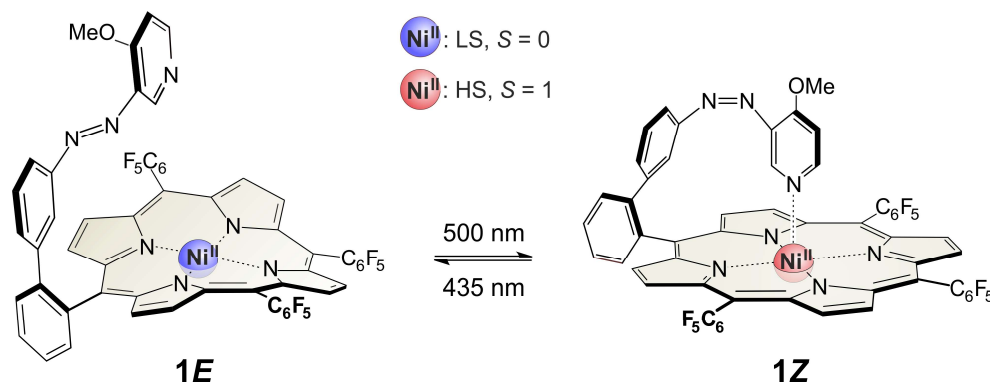


Figure 1: Structures of the azo-functionalized Ni-porphyrin spin switch states.

To gain insight into the ensuing photoswitching mechanisms, we have investigated the ultrafast dynamics of the *E* (low spin) and *Z* (high spin) states of **1** using femtosecond transient absorption spectroscopy after excitation in the Q and B bands of the porphyrin. The four-coordinate low-spin species was found to exhibit virtually identical dynamics as the plain Ni-porphyrin complex. Transient spin state switching happens in <0.25 ps, but a stabilization to the long-lived high spin product is very inefficient, making this channel a very minor one. In contrast, the five-coordinate high-spin compound shows virtually immediate (<0.25 ps) formation of the low-spin product, subsequent vibrational cooling in ~ 12 ps, and persistent positive low-spin product absorption at 1 ns. The high-spin-to-low-spin quantum yield is $\sim 6 \pm 1$ %. The photoinduced dynamics are dominated by coupling of the porphyrin- $\pi\pi^*$ and Ni(d-d)/Ni(d^2) states, not by initial photoisomerization of the azopyridine. The ligand *cis-trans* isomerization may instead take place in the azopyridine triplet state reached via the porphyrin triplet.

References:

[1] S. Venkataramani, U. Jana, M. Dommaschk, F.D. Sönnichsen, F. Tuczec, R. Herges, *Science* **331**, 445 (2011).