

Ultrafast dynamics of a bi-stable azopyridine Ni-porphyrin spin switch after photoexcitation in the porphyrin B-bands

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Abstract. Femtosecond time-resolved absorption measurements of a magnetically bi-stable azopyridine Ni-porphyrin in solution at room temperature show that the photo-induced dynamics are dominated by transient low-spin \rightleftharpoons high-spin interconversion involving Ni (d^2) and (d, d) states.

1 Introduction

Metal porphyrins are naturally occurring chromophores that play central roles in a multitude of biological processes such as photosynthesis, redox reactions or oxygen transport [1]. Many of their fascinating functions are initiated by absorption of light. An extraordinary example is the recently designed nickel porphyrin spin-state switch (azoNiPor) with an azopyridine unit attached to the porphyrin ring (Fig. 1a), which shows magnetic bi-stability in solution at room temperature and thereby carries potential as photo-switchable contrast agent for magnetic resonance imaging (MRI) [2, 3]. As illustrated in Fig. 1 (b–d), the central Ni(II) ion can be converted almost quantitatively from the diamagnetic singlet low-spin (*LS*) to the paramagnetic triplet high-spin (*HS*) state by irradiation with green light at $\lambda = 505$ nm. In this process, the pyridine nitrogen coordinates axially to the Ni centre, when the azo arm is switched from the *trans* to the *cis* configuration. The spin-state transition is reversed upon irradiation with blue light at $\lambda = 435$ nm.

Here, we report on a study of the ultrafast photo-induced dynamics of the azoNiPor switch in its *LS-trans* and *HS-cis* states following excitation in the B (Soret) bands of the porphyrin by means of femtosecond time-resolved transient absorption spectroscopy to shed light onto the spectro-temporal processes and physical mechanisms behind the spin-state switching.

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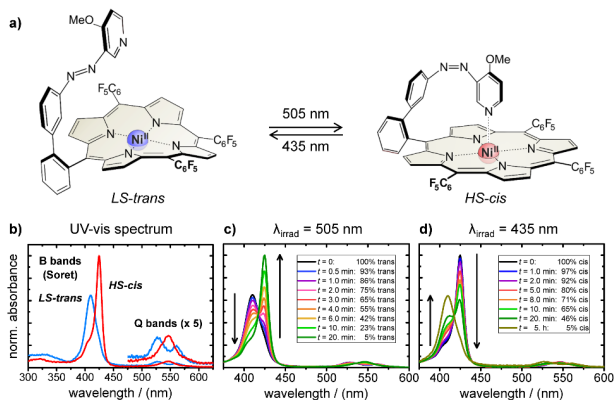


Fig. 1. a) Structures of the azoNiPor spin switch in its *LS-trans* and *HS-cis* forms; b) static UV-Vis spectra; c) conversion of the *LS-trans* to the *HS-cis* form by cw irradiation at $\lambda = 505$ nm (12.4 mW, 30 nm bandwidth); d) conversion of the *HS-cis* to the *LS-trans* form by cw irradiation at $\lambda = 435$ nm (0.066 mW, 5 nm bandwidth).

2 Experimental details

The femtosecond transient absorption measurements were performed in solution in cyclohexane in flow cells of 0.1 and 1 mm optical path length [4]. The samples were excited by pump pulses at $\lambda = 406$ nm (*LS-trans*) and 420 nm (*HS-cis*), respectively, and interrogated by supercontinuum probe pulses from 350 – 700 nm.

3 Results and discussion

The observed transient spectra of the *LS-trans* azoNiPor isomer in Fig. 2 exhibit a pronounced negative band in the 400 – 425 nm region reflecting the ground-state bleach (GSB) and a strong positive excited-state absorption (ESA) from 425 – 450 nm. In the quadratic-planar ligand field of the *LS* state, the d^8 Ni(II) ion adopts its $^1(d_z^2)$ electron configuration with an empty $d_{x^2-y^2}$ orbital. The pronounced ESA thus arises from the Ni $^3(d_z^2, d_{x^2-y^2})$ state. The apparent first derivative-like transient band shape that is typical for these dynamics [5] is fully established after $\Delta t \sim 3$ ps (cf. Fig. 2c). The optically excited S_2 ($^1\pi\pi^*$) state of the porphyrin evidently undergoes ultrafast intersystem crossing (ISC) in <100 fs. The high vibrational energy dumped into the molecule by the accompanying Ni $^1(d_z^2) - ^3(d_z^2, d_{x^2-y^2})$ transition explains the initially very broad ESA up to ~ 550 nm, but the band rapidly blue-shifts and narrows by vibrational cooling on a time scale of $\tau \sim 1$ ps. All transient spectral features eventually decay, indicating a virtually complete ground state recovery (GSR) with $\tau \sim 350$ ps (Fig. 2d).

The axial azopyridine in the *HS-cis* isomer raises the energy of the Ni (d_z^2) orbital such that the Ni electron configuration switches to $^3(d_z^2, d_{x^2-y^2})$ and the porphyrin S_2 ($^1\pi\pi^*$) band red-shifts to 420 nm. The transient spectra after 420 nm excitation in Fig. 2 display second derivative-like band shapes due to the characteristic transient absorption by the *LS* state around 406 nm. After the initial optical excitation to the Por(S_2)–Ni $^3(d_z^2, d_{x^2-y^2})$ state, the

system thus reverts at least partially to a Por–Ni¹(d_{z²) state, which repels the axial azo ligand. At $\Delta t \sim 11.9$ ps, the absorbance at 406 nm indicates a transient *LS* state yield of ~ 20 %. Subsequent relaxation processes, however, lead to recapture of the azo ligand and efficient *HS-cis* GSR. The slow ($\tau \sim 600$ ps) temporal decay asymptotically extrapolates to an *LS* yield of ~ 6 % as upper limit. Actinometric quantum yield measurements at 425 – 435 nm established a value of 2.2 ± 0.2 %.}

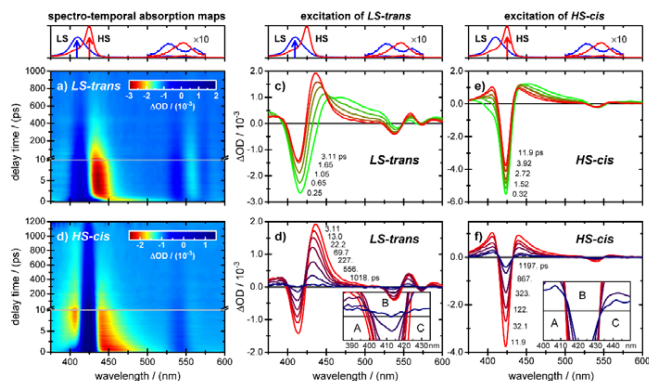


Fig. 2. Measured spectro-temporal transient absorption maps of the change in optical density ΔOD after fs excitation of azoNiPor in its *LS-trans* (a) and *HS-cis* forms (b) and selected transient spectra at different delay times (c – f).

Additional measurements are in progress to shed light on the photo-induced dynamics after excitation of both azoNiPor isomers in the Q bands and in the mysterious 450 – 500 nm window, where *LS*-to-*HS* conversion takes place (Fig. 1b). We speculate that spin-state switching at 500 nm is mediated by transfer from the “hot” ³[Por–Ni(d²/d)] state right after excitation to the azopyridine triplet state, where *trans-cis* isomerization is easily feasible. The measured *LS*-to-*HS* quantum yield at 500 nm is very low (~ 0.5 %). Direct excitation of the weak azo (*mπ**) band could also contribute to this quantum yield. Despite the low quantum yields, the azoNiPor system stands out for the almost quantitative *LS* \rightleftharpoons *HS* interconversion. The excellent overall spin-state switching efficiency is mediated by the huge absorption coefficients of the porphyrin.

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