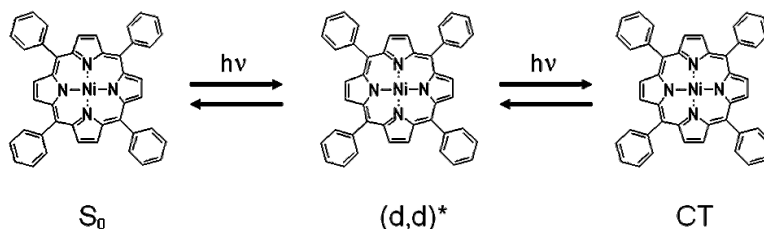


Two-Pump–One-Probe Femtosecond Studies of Ni(II) Porphyrins Excited States

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Two-Pump–One-Probe Femtosecond Studies of Ni(II) Porphyrins Excited States

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Tetrapyrrole macrocyclic ligands (e.g., porphyrins) have a set of highly delocalized π -orbitals situated on the carbon–nitrogen framework. When such a ligand is coordinated to a centrally located metal atom of the transition series, having incompletely filled d-orbitals (Ni, Co, Fe, Cu, etc.), the π - and d-manifolds can interact. As a result, the excited state deactivation dynamics becomes very dependent on the electronic nature of the central metal. For example, Ni(II) porphyrins rapidly form a metal-centered (d,d)* state after photoexcitation into the Soret or Q-bands,^{1,2} and the radiative process is suppressed very effectively ($\Phi < 10^{-5}$).³ The results of extended Hückel calculations and the weak fluorescence support the suggestion that the normally emissive (π,π^*) excited state of the porphyrin macrocycle deactivates to produce a lower-lying singlet or/and triplet metal centered (d_z^2 , $d_{x^2-y^2}$) excited state.^{3,4} Rodriguez et al.^{5–7} showed that common nickel porphyrins such as nickel(II) *meso*-tetraphenylporphyrin (NiTPP) and NiOEP undergo $\pi^* \rightarrow d^*$ crossing within ca. 1 ps. The d^* state repopulates the ground state with lifetime of 200–500 ps.^{1,8} Because of symmetry restrictions, the ($d_z^2 \rightarrow d_{x^2-y^2}$) transition is forbidden and transitions between d states are optically silent.

The $\pi^* \rightarrow d^*$ energy transfer generates a porphyrin molecule with a ground state π -system and an excited metal center. The electronically changed metal center serves to produce spectral shifts in the ground state absorption spectrum of the porphyrin,^{1,2,6} but the intrinsically high extinction coefficients are not significantly affected by the metal center configuration, as evidenced by a symmetric derivative shape of the difference absorption spectra.^{2,6} Thus, following the initial pumping photon pulse with a second one, delayed by a few picoseconds, will generate an S_1 (π -localized) state with d-electron configuration different from the S_1 (π -localized) state formed by the first photon pulse. It is interesting to elucidate the mechanism of deactivation of such a doubly excited state, and to do this femtosecond two-pump–one-probe transient absorption experiments have been employed.

The molecules chosen for this study were NiTPP and nickel(II) *meso*-tetra(4-sulfonatophenyl)porphyrin (NiTPPS). The dual excited state deactivation dynamics of NiTPPS were studied in deionized water and dimethyl sulfoxide (DMSO), whereas NiTPP was studied in toluene. The excitation wavelengths of 400 and 550 nm were used to generate the S_2 and S_1 states of the π -system, respectively. For NiTPPS in DMSO, the first pulse (400 nm) converted the porphyrin π -system into the $S_2(\pi,\pi^*)$ state, which produced the $S_1(\pi,\pi^*)$ state within the instrument response time (ca. 130 fs). The $S_1(\pi,\pi^*)$ state decayed to form the metal centered excited (d,d)* state that vibrationally relaxed within 14 ps. The difference absorption spectrum of this state is shown as the red curve (40 ps) in Figure 1. The lifetime of the (d,d) excited state was 470 ps.⁹ The second (550 nm) pulse selectively (4:1) targeted the $S_0 \rightarrow S_1$ transition of those molecules that had an excited metal center. The selectivity was based on the fact that the (d,d)* excited Ni(II)

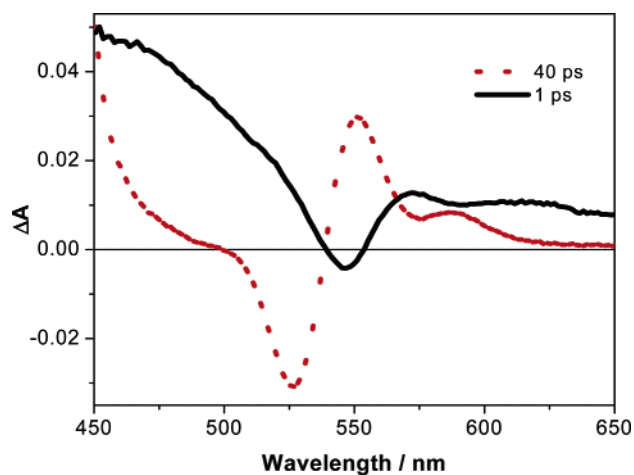


Figure 1. Transient spectra of the Ni(II)TPPS in DMSO. The dotted red line was recorded at 40 ps after the first pulse; the black solid line is the first observed transient after the second pulse.

porphyrin molecules absorb ~ 4 times stronger at 550 nm than the Ni(II) porphyrin molecules in their ground states. This is because the (d,d)* state produced by the first excitation pulse slightly shifts the ground spectrum of the porphyrin^{1,2,5} (in this case into the red) because of the changed central metal electron configuration.

This new absorption spectrum becomes the reference spectrum (or pump-off spectrum) in the two-pump–one-probe experiment. The second pulse (550 nm) was delivered to the sample approximately 40 ps after the first excitation event. At this time, the ground state of the tetrapyrrole π -system was already regenerated and the excitation was localized at the metal center. The transient spectrum of the NiTPPS in DMSO after two successive excitation pulses (400 and 550 nm) is shown in Figure 1. The spectrum taken at a 1-ps probe delay corresponds to the first observed transient. It showed a positive broad absorption band at around 480 nm, bleaching centered at 548 nm, and a positive band peaking at 575 nm. After a few tens of picoseconds post-pulse 2 the absorption had decayed to the pre-pulse baseline level. This behavior indicates that the first pulse converts all ground states to excited states; if not, the second pulse would have generated an additional concentration of d,d states that would have shown up as a derivative-shaped spectrum at the longer times. The kinetic profile at 480 nm showed an instrument limited rise and a biexponential decay with lifetimes of 0.6 and 4 ps (Figure 2). Similar behavior was observed for the kinetic trace at 575 nm.

Those states populated by the second pulse with excitation in both π and d manifolds (designated $S(\pi^*,d^*)$) must deactivate through a channel different from the normal S_1 state (designated $S(\pi^*,d)$), viz. $S(\pi^*,d) \rightarrow (\pi,d^*) \rightarrow S_0$, because the (d,d)* state is already populated. A possible pathway would be the direct (radiative) deactivation into S_0 , similar to that of Zn porphyrins.¹⁰

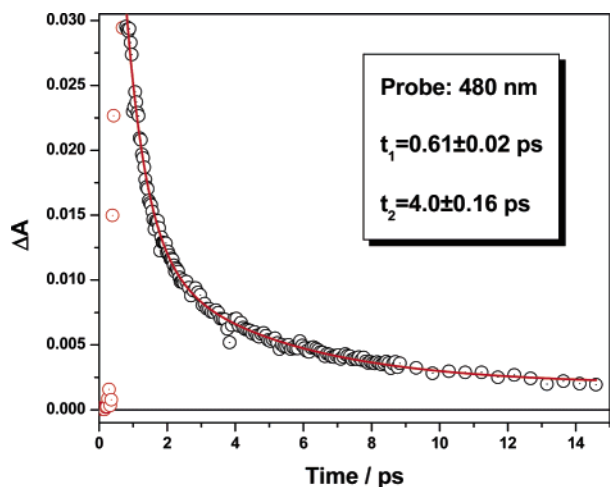


Figure 2. Kinetic profile of the NiTPPS transient absorption at 480 nm. Solvent: DMSO.

This possibility can be ruled out because the intrinsic $S_1 \rightarrow S_0$ lifetime in such porphyrins is on the order of a few nanoseconds.

This is significantly longer than the 0.6 and 4 ps lifetimes observed here. Additionally, the lack of luminescence from the dual excited state also points out to a deactivation pathway different from the direct $S_1 \rightarrow S_0$ route within the π -manifold.

Another possibility is the formation of an intramolecular charge transfer state. To find further support for this, we investigated the dually excited state deactivation dynamics of NiTPPS in water as a more polar solvent. In water, similar spectral data were found, and the first decay component at 480 nm remained virtually unchanged (0.7 ps), whereas the second component became slower (10 ps).

Such increase in the reverse process lifetime is often observed for charge transfer states, whose recombination usually lies in the inverted region of the Marcus curve and is inhibited in a more polar solvent.^{11,12} The small solvent effect on the charge separation rate is not surprising. First, subpicosecond electron transfer is too fast to be affected by the nuclear motions of the polar solvent molecules, which occur on the 10^{-11} – 10^{-9} s scale. Additionally, the fast (10^{-15} s) electronic motions in the solvent molecules have a significantly weaker stabilization effect and are not directly related to the solvent polarity.^{13–16}

The electronic configuration of the four lowest d orbitals in the excited Ni (d,d) state is identical to that of the ground state of Co(II). This suggests that the deactivation of the S_1 in (d,d)* excited Ni porphyrin could be similar to deactivation of the π -localized S_1 state in a Co(II) porphyrin. Moreover, Co(II) has a d^7 electronic configuration, and the odd d_{z^2} electron interacts with the porphyrin π -system to produce doublets and quartets.¹⁷ Iterative extended Hückel calculations predict a low-lying (π ,d) charge transfer state, which is a result of intramolecular electron transfer from the porphyrin ring to the metal center: $a_{2u}(\pi) \rightarrow Co(d_{z^2})$.¹⁷ Yu et al. have shown that deactivation of the Co(II)TPP S_1 state occurs through the formation of the above charge transfer state.¹⁸ The lifetimes for the charge separation and recombination processes in benzene were reported to be 1.8 and 16 ps, respectively.¹⁸ It should be noted that the NiTPPS doubly excited state lifetimes resemble

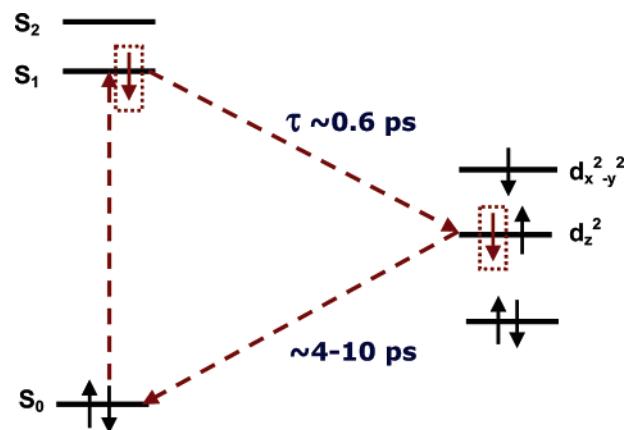


Figure 3. Proposed scheme for the deactivation of Ni(II) porphyrin dual excited state. The black arrows indicate the electronic configuration of the molecule immediately before the second excitation pulse. The red arrows show the electronic transitions caused by the absorption of the second photon.

the kinetics reported for Co(II)TPP. Additionally, Yu et al. reported that the lifetimes of the Co(II)TPP charge separation state increased with solvent polarity. This agrees with our observation.

Dual photoexcitation of NiTPP in toluene produced the transients and decay dynamics very similar to those observed for NiTPPS.¹⁹ These findings suggest that the NiTPP and NiTPPS doubly excited states follow the same deactivation mechanism.

On the basis of the above data, we have proposed the mechanism in Figure 3 involving the formation of an LMCT state for the Ni(II) porphyrins dual excited state deactivation.

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Supporting Information Available: Experimental setup. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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