

## Photoaddition of Psoralens to DNA traced by Time-Resolved Spectroscopy

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Psoralens are known for their application in the PUVA therapy (psoralen + UV-A irradiation).<sup>[1]</sup> This therapy is used to treat widespread skin diseases such as psoriasis and vitiligo. Their pharmaceutical activity is attributed to DNA intercalation followed by an UV-induced [2+2] cycloaddition (see Fig. 1). Our attempts to trace this reaction by time resolved spectroscopy revealed an electron transfer (ET) process competing with the photoaddition.<sup>[2,3]</sup> In these studies, the DNA base guanine was identified as the donor in the ET process.<sup>[3]</sup> Therefore, in the following experiments AT only DNA double strands were used. The psoralen derivative AMT (see Fig. 1) intercalated in AT-DNA features a singlet lifetime of 1 ns. The triplet state persists for 6  $\mu$ s. These values are comparable to the ones of non-intercalated AMT.

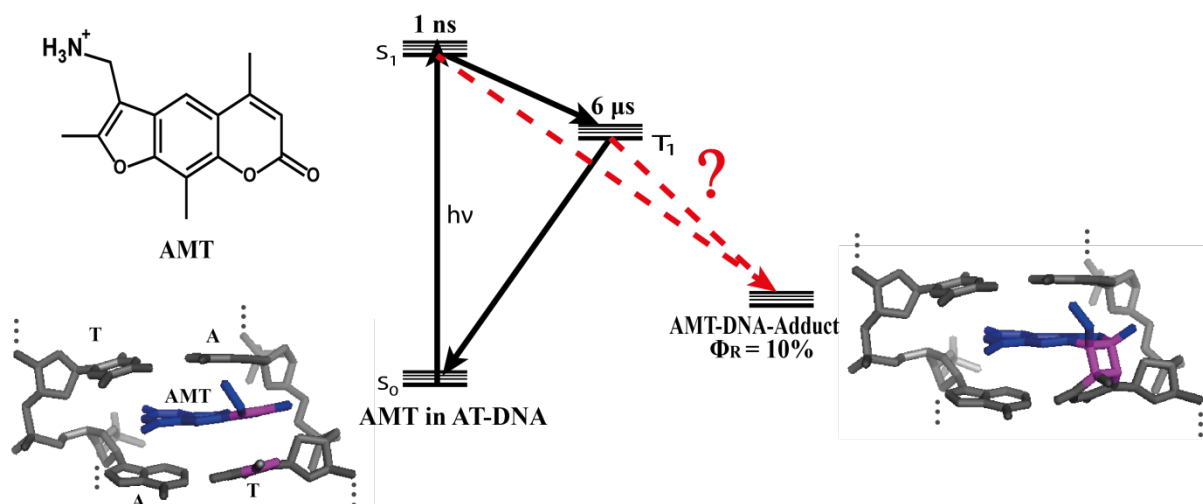


Figure 1. Psoralen derivative 4'-aminomethyl-4,5',8-trimethylpsoralen (AMT) intercalates into DNA (left). Upon irradiation with UV-light it binds to the DNA (right).

UV/VIS signatures clearly reveal the presence of the photoadduct after the decay of the triplet state. Due to overlapping signal contributions, however, it is still ambiguous whether it is formed within 1 ns or 6  $\mu$ s, that is, from the singlet and/or triplet state. Making use of the generally more characteristic patterns of vibrational spectroscopy, we currently work on tracing the addition by time resolved IR-spectroscopy. The adduct formation leaves strong signatures in the infrared spectrum, which will allow us to identify the precursor state of the adduct.

**References:**

- [1] N. Kitamura, S. Kohtani, R. Nakagaki, *J. Photochem. Photobiol. C*, **2005**, 6, 168-185
- [2] S. Fröbel, A. Reiffers, C. Torres Ziegenbein, P. Gilch, *J. Phys. Chem. Lett.*, **2015**, 6, 1260-1264
- [3] S. Fröbel, L. Levi, S. M. Ulamec, P. Gilch, *ChemPhysChem*, **2016**, 17, 1377-1386