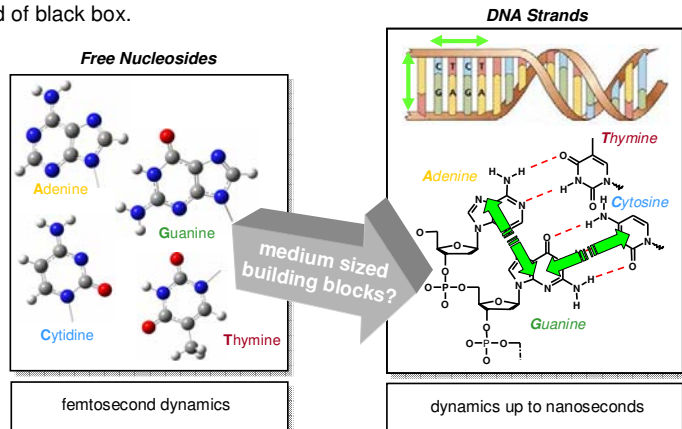
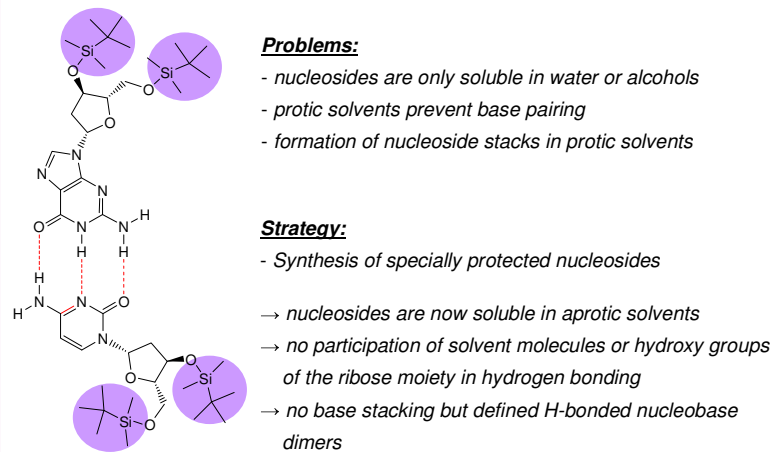


Motivation & Aims

The DNA encodes the genetic information and is therefore the most important biomolecule for the reproduction of life. Yet the available information on the electronic properties and excited state dynamics is still very limited. Time-resolved data on medium sized building blocks, especially on hydrogen bonded nucleobase pairs are virtually missing and remain as a kind of black box.

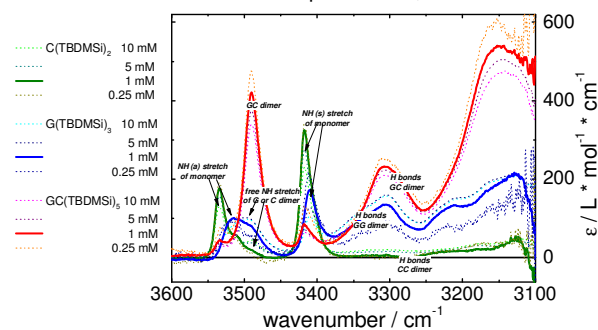


Here, we report on the first femtosecond time-resolved experiments on the the GC Watson-Crick base pair in solution to determine the effect of hydrogen bonding on the excited state lifetime.

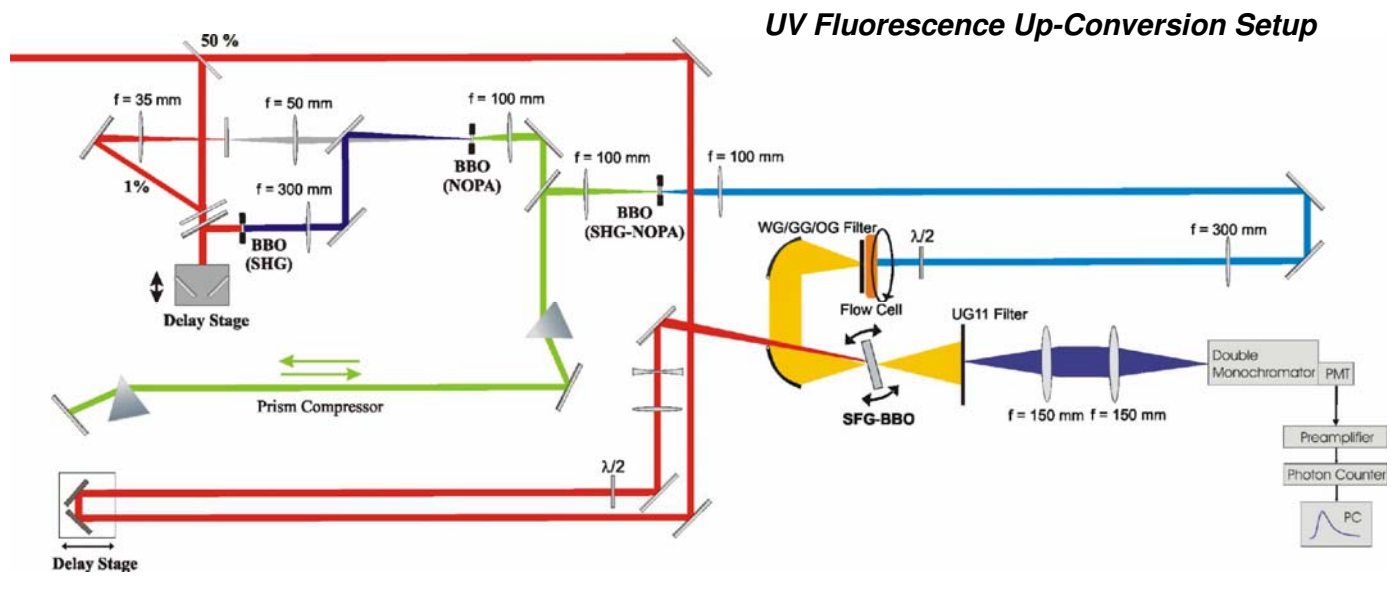
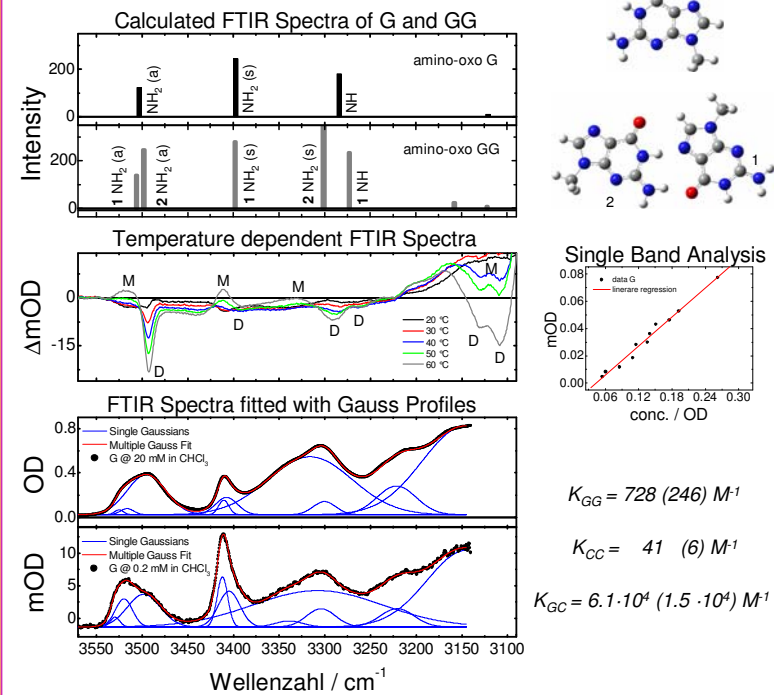


Characterisation of the H-bonded Base Pairs

Static FTIR Spectra of G, C and GC

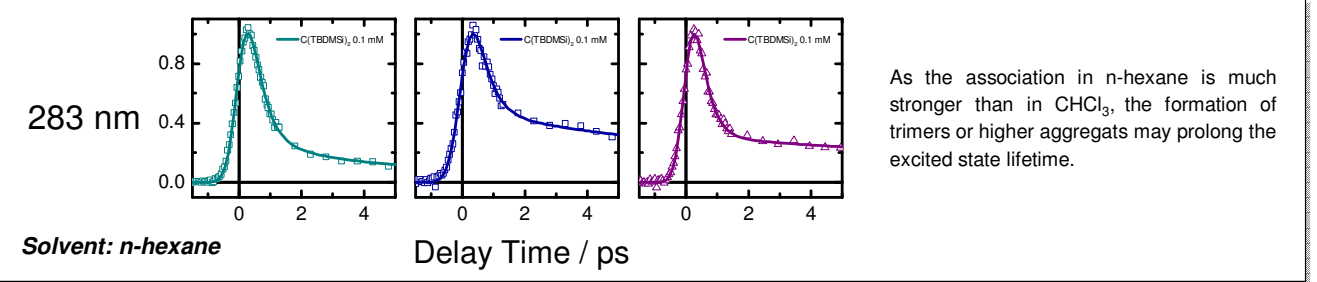
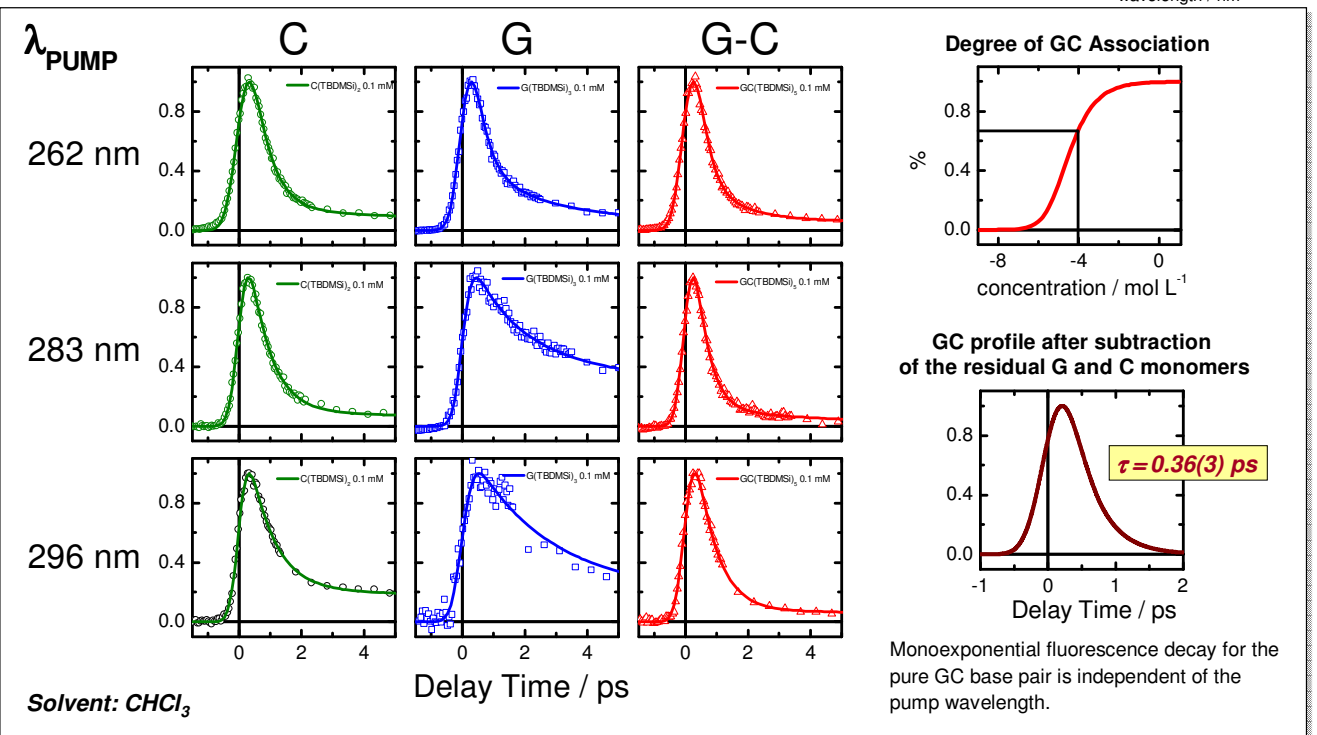
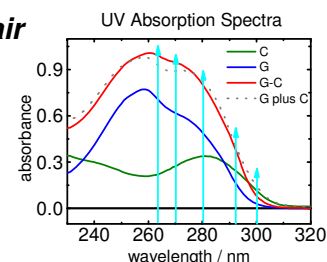


- Static FTIR measurements of the G and C monomers, homo- and heterodimers in a concentration range between 0.25 – 150 mM.
- Multiple Gaussian Band Fitting of each spectral trace.
- Assignments of bands were supported by G3B3 (rel. energies of tautomers) and DFT-PW91 (frequencies of the free nucleosides and H-bonded dimers) calculations.

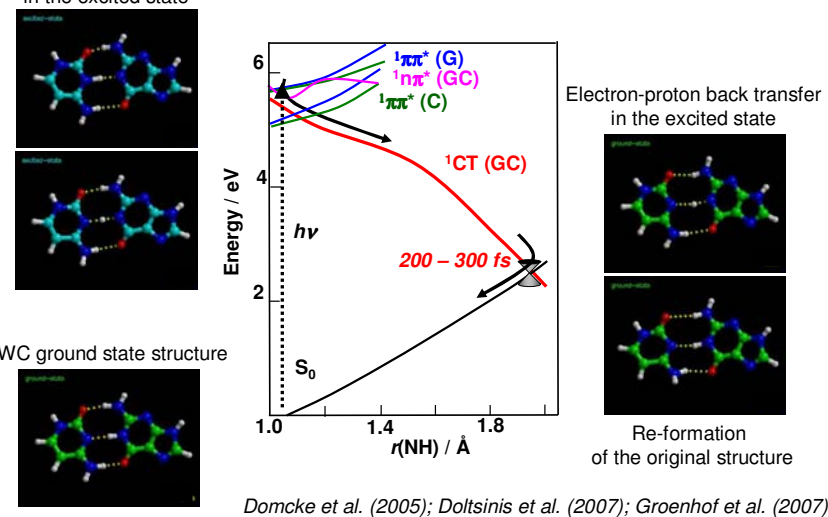


Fluorescence Decay Profiles of G, C and the GC Watson-Crick Base Pair

- The excitation wavelength was tuned between 258 nm and 302 nm.
- The emission/detection wavelength was set to 350 nm (~ emission maximum).
- The pump energy was  $\leq 0.05 \mu J$ .
- The concentration varied between 0.01 and 1 mM, whereas here the results at 0.1 mM are presented:



Coupled electron-proton transfer in the excited state



Conclusion & Discussion

- Our results unambiguously demonstrate that the excited state lifetime is reduced by complementary hydrogen bonding in the WC base pair in solution.
- This is the first direct measurement of the effect of H-bond formation.
- The effect is stronger on G than on C.
- The findings point at a unique ultrafast optically dark relaxation pathway.
- The pathway might be a theoretically proposed coupled electron-proton-transfer in the excited state that is exclusively accessible in the Watson-Crick form, where it leads to a barrierless ultrafast relaxation back into the ground state.
- Calculated excited state lifetimes agree very well with our measured lifetime of 0.36(3) ps.