

## Microfluidic Mixer for Ultrafast Spectroscopy on Unstable Compounds

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We demonstrate a method to measure the ultrafast dynamics of reactions that can undergo a very fast thermal reaction in competition to the photoinduced one of interest. To achieve this we combine of a fast mixing microfluidic chip with broadband spectroscopy on the fs- to  $\mu$ s-timescale<sup>[1,2]</sup>. The reaction solutions are mixed on the chip and the ultrafast dynamics is recorded before the substance has a chance to degrade. This method allows to study a whole new field of photochemical/photobiological reactions or non-equilibrium systems<sup>[3]</sup>.

The microfluidic mixer (Fig. 1) is designed for rapid mixing and to match the requirements of ultrafast spectroscopy. The chip is made of three layers fused silica, where the middle layer of 250  $\mu$ m thickness has the channel etched in and connectors on the front window. The chip was built with specially designed channels by Translume Inc. (Ann Arbor, Michigan, USA). Fused silica as compared to the frequently used plastic chips has the advantage of good optical quality, transparency in the UV and high damage and chemical resistance.

The inlet channels (300  $\mu$ m width) are brought together in an cross-mixer and flow through several "F"-shaped structures. These structures accelerate the mixing by using lamination and chaotic advection<sup>[4]</sup>. The laminar flow is split in the middle and again merged on top of each other in the next "F" that is out of plane. This increases the number of surfaces between the two solutions, and while diffusion is generally slow, this makes best use of it. After every two "F"-structures a window of 300x300  $\mu$ m is applied for the laser pulses and the measurement.

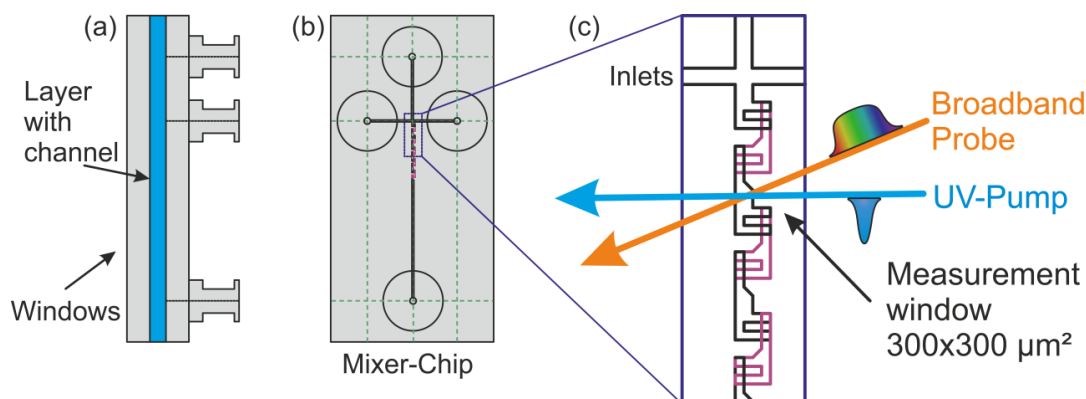


Figure 1. Microfluidic mixer chip. a) Cross section b) Front view c) Enlargement of the mixing structures. Violet structures are out of plane, etched into the back window. Channel depth is 250  $\mu$ m.

The characterization of the mixing characteristics was done by a color change reaction of a solvatochromic dye and the known ps reaction dynamics of diphenylmethyl (benzhydryl) compounds (Fig. 2) in solvent mixtures of acetonitrile and alcohols. At the second measurement window practically a complete mixing is achieved. At substance conserving flow rates this can be reached by the solution in 100 ms. A flow rate of 125  $\mu$ m/ms is also sufficient to guarantee sample exchange for every laser shot on a 1kHz system. At higher flow rates the mixing improves and it can also be measured at position one, which can be reached in 3 ms. Substance usage at moderate flow rates is for the example of a molecule with  $\epsilon = 5000 \text{ Lmol}^{-1}\text{cm}^{-1}$  roughly 1 mg per hour, at a mixing ratio of 95/5 solvent/reaction mixture.

Benzhydryl-chlorides undergo a C-Cl bond cleavage after UV-excitation. The resulting radical and ion pairs are investigated with ultrafast spectroscopy<sup>[5,6]</sup>. Benzhydryl cations can react ultrafast with alcohols on the ps timescale. On the other hand, the precursor chlorides can undergo a spontaneous thermal solvolysis reaction with the alcohol<sup>[7]</sup>. Depending on the precursor reactivity the half-life in pure methanol can be low as a few minutes to less than a ms and the photoinduced reactions ranges from ps to ns. This is difficult to impossible to measure with conventional methods.

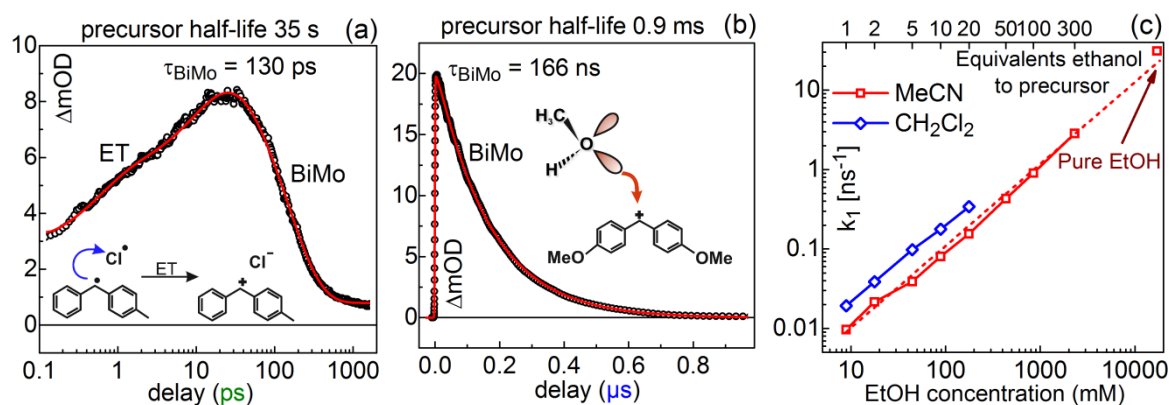


Figure 2. a) Cation signal of methylated benzhydryl b) Cation signal of a dimethoxylated benzhydryl  
c) Reaction rate for the bimolecular reaction in solvent mixtures

Combining microfluidic mixing and ultrafast spectroscopy we were able to measure the reaction dynamics. The precursor dissolved in water-free acetonitrile are mixed on the chip with methanol at a ratio of 95/5 MeOH/MeCN. The excitation wavelength is 270 nm. For a precursor with a half-life of 35 s we observe an initial increase of the cation signature due to electron transfer in the radical pairs and subsequent the reaction with methanol on the ps timescale (Fig. 2a). It was also possible to measure the reaction time of a precursor, that has a very low half-life time of 0.9 ms in methanol, on the  $\mu$ s timescale (Fig. 2b). Additionally, we investigated the influence of the reaction mixture. The dependence on the alcohol concentration is almost perfectly linear. Lowering the polarity of the non-reactive solvent accelerates the reaction (Fig. 2c).

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