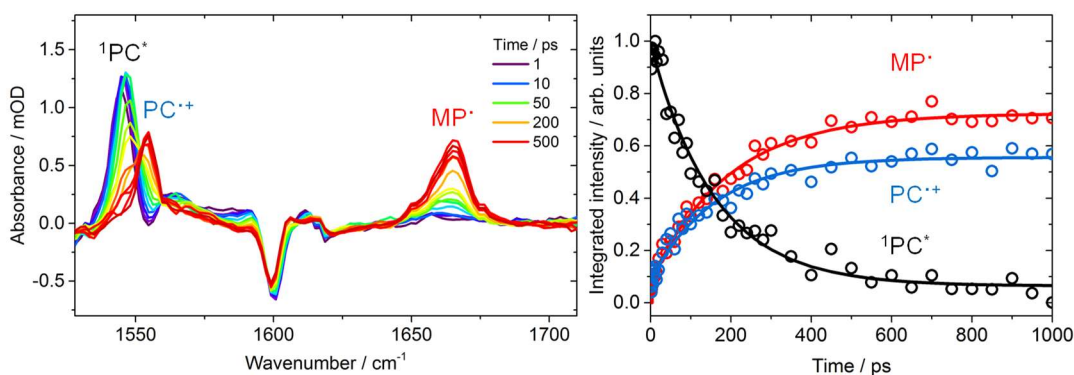


Ultrafast spectroscopy of photocatalysed radical reactions and spin-changing dynamics

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Radical reactions can be valuable in organic synthesis, but unwanted propagation and chain-transfer reactions limit their widespread use. Photoredox catalysis offers a method of controlling radical reactions, and has found recent application in atom transfer radical polymerization to prepare polymers of controlled molecular weight and low size dispersity. Here, we illustrate the use of transient absorption spectroscopy to follow several sequential steps in a photoredox catalyzed reaction over sub-picosecond to nanosecond timescales. We examine the consequences of structural modification of the photocatalyst and choice of solvent.



Transient IR absorption spectra of a 2.1 mM solution of 5,10-di(4-trifluoromethylphenyl)-5,10-dihydrophenazine photocatalyst (PC) and 1.8 M methyl 2-bromopropionate (MBP) in dichloromethane solution (left), and time-dependence of the indicated band intensities (right). PC^{•+} denotes the radical cation of the photocatalyst after electron transfer and MP[•] is a methyl propionate radical produced by dissociative electron transfer to MBP.

We also report 2DIR studies of the exchange dynamics between two isomers of a pentavalent cobalt nitrosyl complex in dichloromethane. The fluxional complexes exchange between linear and bent coordination of the NO ligand on timescales of a few picoseconds. This structural isomerization is accompanied by a change between low (singlet) and high (triplet) spin configurations, and provides an unusual example of fast intersystem crossing between regions of singlet and triplet spin character on the lowest adiabatic electronic potential energy surface [2].

References:

- [1] D. Koyama, H.J.A. Dale and A.J. Orr-Ewing, submitted (2017).
- [2] H.J.B. Marroux et al., submitted (2017).