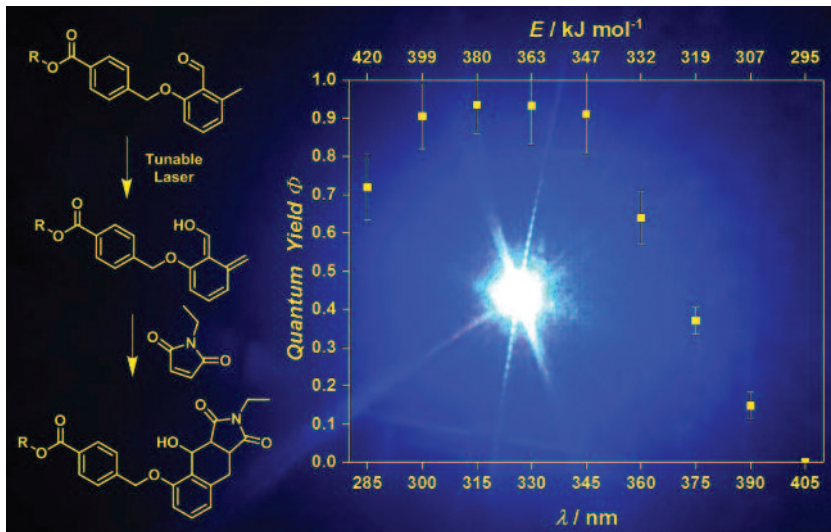


# Light, reactivity, action!

Efficient light-induced ligation protocols are valuable tools for functional materials design. The teams of Christopher Barner-Kowollik and James Blinco, at the Queensland University of Technology and the Karlsruhe Institute of Technology, Germany, and Michelle Coote at the Australian National University have investigated two highly efficient photoligation reactions involving photoenols and nitrile imines in a combined experimental and theoretical study (Menzel J.P., Noble B.B., Lauer A., Coote M.L., Blinco J.P., Barner-Kowollik C. *J. Am. Chem. Soc.* 2017, **139**, 15 812–20).

A unique tunable laser system was used to irradiate samples containing either *o*-methylbenzaldehydes or diphenyltetrazoles and *N*-ethylmaleimide at varied wavelengths and constant photon count to produce action plots of reactivity versus wavelength. The quantum yield of the nitrile-imine-mediated tetrazole ene



cycloaddition was estimated to be higher than  $0.55 \pm 0.06$  at 285 nm, while photoenol-ligation proceeded with quantum yields up to  $0.91 \pm 0.10$ , supporting theoretically established mechanisms via conical intersections. A combination of density functional theory and multi-reference calculations with

precision photochemical analysis provided insight into the mechanisms and optimised reaction conditions for photoligation protocols. These findings will help to design advanced photoresists in which distinct material properties are encoded with different colours of light in 3D laser lithography.