

TAD-AAH! PHOTO-CROSSLINKED MATERIALS AND THEIR ERASING BY WATER OR DARKNESS

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1,2,4-Triazoline-3,5-diones (TADs) are a unique class of reagents that have found a vast array of applications across multiple research disciplines; most notably in organic synthesis, bioconjugation and polymer science.[1] Referred to as the most reactive dienophiles that are to be isolated, TAD-based conjugation reactions are often highly exergonic at ambient temperatures (and far below, e.g. at -78 °C) and swiftly proceed without the need of a catalyst in less than seconds, even with macromolecular substrates. This extraordinary reactivity of TADs was even found to be enhanced under visible light irradiation, making them also susceptible towards dearomative cycloadditions, H-abstractions and even undergoing a self-polymerisation to give a rare nitrogen-backboned photopolymer. In contrast to the wide variety of ‘thermal’ modes of reactivity, these photochemical TAD reactions are only scarcely reported and in fact remained unexplored in a polymer material context.

In this lecture, our latest investigations into the photo-reactivity of TAD compounds and their valorisation into material science will be highlighted. For example, a new type of photoresist has been developed that operates through a backbone crosslinking of poly(ethylene glycol) (PEG) to access macroscopic gels under green LED irradiation that are stable in organic media but readily degrade upon the addition of water.[2] Interestingly, this photoinduced curing of PEG with TADs is also applicable to multiphoton laser lithography ($\lambda > 700$ nm), hence providing access to 3D laser printed microstructures that vanish when immersed in water at 37 °C with varying erasing times. We further explored TAD-based photo-cycloadditions with naphthalenes in order to design so-called ‘light-stabilised dynamic materials’ (LSDMs), i.e. covalently photo-crosslinked materials that can be stabilized under continuous irradiation, yet can be transformed into a viscous liquid by perhaps the mildest trigger of all: darkness.[3-5].

[1] K. De Bruycker, *et. al.*, *Chem. Rev.*, **2016**, 116, 3919.

[2] H.A. Houck, *et. al.*, *Adv. Mater.*, **2020**, 32, 2003060.

[3] H.A. Houck, *et. al.*, *J. Am. Chem. Soc.*, **2019**, 141, 12329.

[4] C.W. Schmitt, *et. al.*, *Polym. Chem.*, **2021**, 12, 449.

[5] D. Kodura, *et. al.*, *Chem. Sci.*, **2021**, 12, 1302.