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Controlling Selectivity in HMF Oxidation with CTF Photocatalysts

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PURPOSE OF THE ABSTRACT

The ongoing endeavour towards more sustainable chemical processes drives research in photocatalysis. Hereby, covalent triazine-based frameworks (CTFs) - a class of porous organic polymers - excel as photocatalysts due to their chemical and thermal robustness, their highly conjugated and nitrogen rich nature, facile syntheses, and most important unprecedented structural variability. This allows the design of tailor-made photocatalysts. [1]
In this work, we present how a controlled modification of the CTF network switches the selectivity of 5 hydroxymethylfurfural (HMF) oxidation into valuable biomass-based molecules which can substitute oil-based products in existing value chains.[2,3] Two reaction mechanisms can be chosen by the choice of the CTF's building block: Either HMF is directly oxidized to 2,5-diformylfuran (DFF) or molecular oxygen is photoactivated to singlet oxygen which reacts in a cycloaddition with HMF to yield 5-hydroxy-5-hydroxymethyl-furan-2-one (H2MF). Extensive characterisation of the optoelectronic properties combined with TD-DFT calculations and detailed investigation of the reaction mechanism allowed us to elucidate this switch in selectivity which adds another tool to the toolbox of CTF photocatalysts.[4]

FIGURES

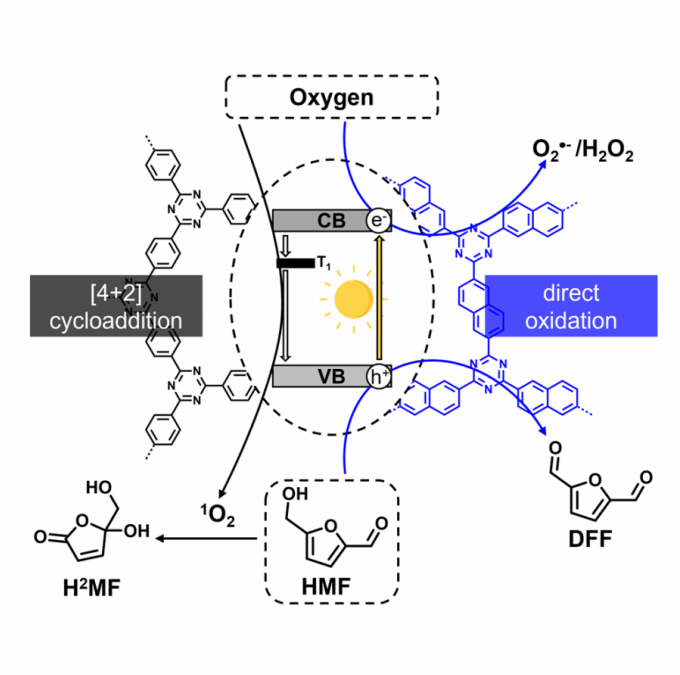

FIGURE 1

Scheme 1

Illustration of direct oxidation of HMF to DFF at CTF surface or subsequent cycloaddition to H2MF after the formation of singlet oxygen.

FIGURE 2

KEYWORDS

Covalent Triazine Frameworks | HMF | Photocatalysis | Oxidation

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