Expanding synthetic cascades using pyridoxal 5'-phosphate (PLP) dependant biocatalysts.

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Biocatalysts (enzymes) are Nature's catalysts that carry out the myriad of metabolic reactions found in every cell. Many natural biocatalysts have been characterised and applied in industry for the sustainable synthesis of various chemicals and pharmaceuticals under mild conditions.[1] One large superfamily of very useful biocatalysts are the pyridoxal 5'-phosphate (PLP)-dependent transaminases (TAs). TAs catalyse the reversible amine transfer between an amine donor and an aldehyde or ketone acceptor to generate either an *R*- or *S*- amine by an accepted mechanism.[2,3] This study explores a well-known TA and its ability to catalyse a novel C-C bond formation reaction using an aminoketone substrate. Spectroscopic analysis has revealed the observation of a novel and long-lived PLP-derived quinonoid intermediate. Current work is focused on studying the substrate range of this new reaction with various nucleophiles and electrophiles.

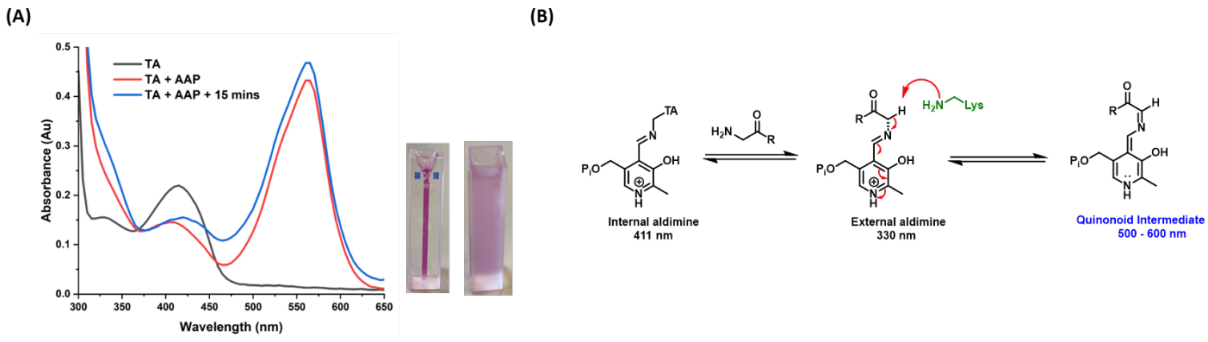

Figure 1. Characterisation of TA substrate binding by UV-Vis spectroscopy. (A) The internal aldimine is formed between the PLP and TA (black). Upon addition of an aminoketone, a new absorbance maximum is observed at 565 nm (red & blue)**. (B)** A proposed mechanism of the binding of aminoketone to TA.

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