## CHROMOPHORE ACTIVATION AT ITS BEST – INFLUENCING THE SELECTIVITY OF PHOTOREACTIONS BY ADDITION OF LEWIS ACIDS

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Enantioselective catalysis of photochemical reactions is a challenge that many groups have faced in recent years. Several approaches have been developed to control the selectivity in the excited state [1]. Among others, it has been shown that chiral Lewis acids can be used to promote enantioselective intra- and intermolecular [2+2] photocycloaddition reactions of enones [2]. However, photocycloaddition reactions of aromatic aldehydes with olefins have not been thoroughly explored. Herein, the intermolecular *ortho* photocycloaddition reaction of phenanthrene carboxaldehyde (1) was studied, with a focus on the use of achiral and chiral Lewis acids in order to influence the selectivity of the reaction [3].



Without Lewis acids both expected products, the *ortho* photocycloaddition product *rac*-**2** and the oxetane *rac*-**3** were formed. The addition of Lewis acids led to an extensive bathochromic shift of the absorption band with  $\pi,\pi^*$  character and therefore selective excitation of the Lewis acid substrate complex was possible. Irradiation of this complex with visible light led to exclusive population of the  $\pi,\pi^*$  state and consequently to the formation of the *ortho* photocycloaddition product **2** as the only photoproduct.

Currently, the photochemical reactivity of 1-naphthaldehyde and 2-naphthaldehyde with olefins is under investigation. It is known that when irradiated with light of short wavelength, both aldehydes only show reactivity at the carbonyl group [4]. However, there are indications that the aromatic ring can be activated by catalytic amounts of Lewis acids and as a result the type selectivity of photoreactions can be reversed.

<sup>[1]</sup> C. Brenninger, J. D. Jolliffe, T. Bach, Angew. Chem. Int. Ed. 2018, 57, 14338-14349.

<sup>[2]</sup> a) R. Brimioulle, T. Bach, Science 2013, 342, 840-843; b) S. Poplata, T. Bach, J. Am. Chem. Soc. 2018, 140, 3228-3231.

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<sup>[4]</sup> a) N. C. Yang, *Pure Appl. Chem.* **1964**, *9*, 591-596; b) A. G. Griesbeck, H. Mauder, K. Peters, E.-M. Peters, H. G. von Schnering, *Chem. Ber.* **1991**, *124*, 407-410; c) S. Fukuzumi, N. Satoh, T. Okamoto, K. Yasui, T. Suenobu, Y. Seko, M. Fujitsuka, O. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 7756-7766.