Poster

Hydrogen bond donating MOFs – synthesis and structure

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Hydrogen-bond-donating (HBD) catalysis has emerged as a biomimetic alternative to Lewis acid activation and it is an effective approach for the synthesis of various highly valuable intermediates for pharmaceutical and agricultural industries. HBD catalysts are capable of binding selectively and activating reactive substrates during the reaction process through hydrogen bonding or other non- covalent interactions [1].

Among these catalysts, urea has been widely utilized as a catalytic moiety owing to its chelating hydrogen bonding through acidic N- H sites. However, the catalytic and orienting effects of H-bond donors present in homogeneous HBD catalysts can be significantly attenuated as a result of self-assembly (catalyst-catalyst interactions leading to the formation of dimers or oligomers (Figure 1a)), leading often to a decrease in catalyst reactivity [2].

Thus, it is necessary to introduce enhanced catalyst loading or elongated reaction time or external toxic additives to achieve high yield in a certain homogeneous catalytic system. Consequently, there is a huge potential for new directions, substrates and opportunities if these catalysts were to be covalently incorporated into coordination polymers, which possess defined reaction environments and high porosity (Figure 1b), and thus prevent self-assembly [3].

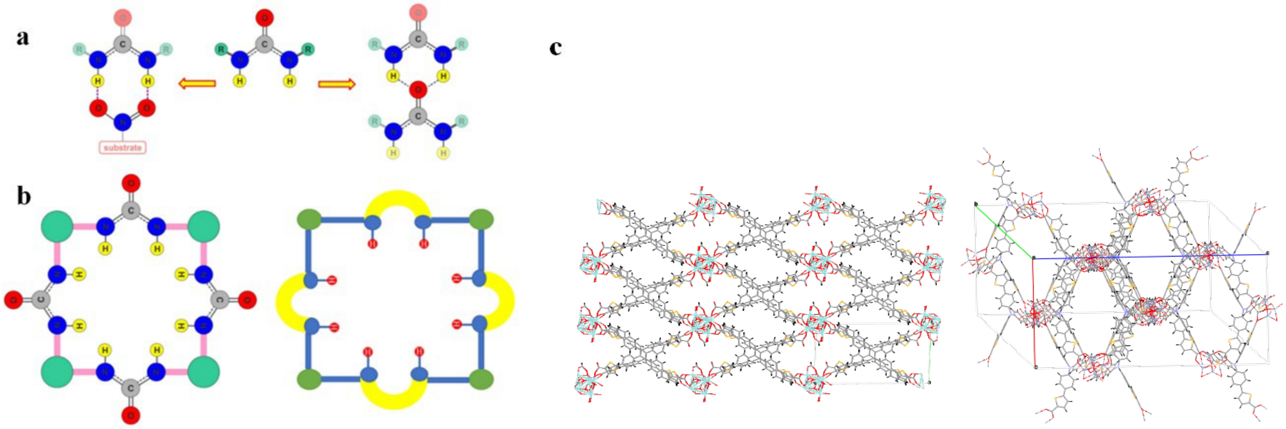

Figure 1. a) example of self-assembly in urea-based catalysts (left: activating electrophilic moieties (e.g., β-nitroalkenes in Friedel–Crafts Reaction) right: catalyst-catalyst interactions leading to the formation of dimers or oligomers, and quenching of cata- lytic activity b) HBD MOF strategy c) new mesoporous urea based MOF structures.

Based on this hypothesis we designed several HBD-group functionalized linkers, which we are now incorporating in MOFs with different non-toxic metals, aiming for large and hexagonal pores, the solid state structures of which we will present here (Figure 1c).

A variety of organic transformations are known to be promoted by HBD catalysts in a racemic or asymmetric fashion, such as Diels– Alder, Mannich, Friedel–Crafts reaction, Michael addition, and protection of alcohols [4]. We next will investigate the catalysis activity of MOF in well-known model reactions with a large number of available literature examples, e.g. Friedel–Crafts reactions between pyrroles and β-Nitroalkenes, and then we will compare their performance with their homogenous analogues. This approach can be further extended for a variety of important organic transformations.

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The authors thank dr. Tobias Stürzer and dr. Carsten Lenzcyk (Bruker AXS Application Centre) for data collection.