From Sustainable Transformations to Supramolecular Approaches in Catalysis

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The generation of more efficient, atom- and step-economy transformations is of primary importance to meet the societal challenges associated the 21st century. In this context, transition metal catalysis is an enabling technology and in our laboratories we have developed a number of sustainable approaches (C-H bond functionalizations, one-pot multi-step sequences, hydrogen production, direct reductive aminations, oxydations, etc.) aiming at minimizing chemical wastes while controlling metal's activity and selectivity.[1] On another hand, we have developed metal-catalyzed transformations which are controlled by remote, kinetically labile interactions taking place in the secondary coordination sphere of the metal catalyst.[2] In particular, we have exploited the reversible binding between nitrogen-containing substrates and metalloporphyrins as a tool for the design of supramolecular catalysts. These supramolecular catalysts feature unique atom-precise selectivities that enables to tackle challenging chemical transformations besides displaying enzyme-like behaviours such as substrate selectivity and Michaelis-Menten kinetics.[3]

[1] Selected examples: (a) *Adv. Synth. Catal.* **2016**, *358*, 3847; (b) *Org. Lett.* **2017**, *19*, 6404; (c) *Catal. Sci. Technol.* **2019**, *9*, 1301 ; (d) *Catal. Sci. Technol.* **2019**, *9*, 4711; (e) *Catal. Sci. Technol.* **2020**, *10*, 180; (f) *Catal. Sci. Technol.* **2021**, *11*, 5772; (g) *Chem. Eur. J.* **2022**, *28*, e202201078; (h) *Angew. Chem. Int. Ed.* e202211016, early view.

[2] *Chem. Soc. Rev.* **2021**, *50*, 3565.

[3] (a) *Chem. Eur. J.* **2017**, 23, 5033; (b) *Chem. Eur. J.* **2019**, 25, 627; (c) *Angew. Chem. Int. Ed.* **2021**, *60*, 18006; (d) *Chem. Eur. J.* **2022**, *28*, e202201970.