

# Structure and Dynamics of Single Chiral Molecule/Prochiral Molecule Complexes on Metal Surfaces: Surface Chemistry in Heterogeneous Asymmetric Catalysis

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Modification of metal surfaces through the adsorption of chiral molecules is a method to create catalytic sites for enantioselective reactions. The chiral molecule is referred to as a chiral modifier by analogy to the term chiral auxiliary used in homogeneous asymmetric catalysis. In this presentation, we will describe combined experimental and theoretical surface studies of individual complexes formed between chiral modifiers and prochiral reactants on a platinum surface. Our work is inspired by the catalysis literature on the enantioselective hydrogenation of activated ketones on cinchona-modified Pt catalysts. Using scanning tunneling microscopy (STM) imaging and density functional theory (DFT) calculations, we probe the structure and relative abundances of non-covalently bonded surface complexes formed between (*R*)-(+)-1-(1-naphthyl)ethylamine and representative prochiral molecules. Each prochiral molecule is found to adopt multiple complexation configurations around the ethylamine group. The structures reveal the hierarchy of chemisorption and, sometimes multiple, H-bonding interactions involved. While the principal intermolecular interaction is NH $\cdots$ O bonding, relative abundances are determined by secondary CH $\cdots$ O or CF $_3\cdots$ H interactions. Submolecularly resolved STM images permit the determination of the prochiral ratio (*pr*) induced by the chiral modifier. Sequential STM measurements on individual fluxional complexes show that binding states can interconvert through prochiral inversion as well as other processes. The complexation state-specific information on structure, prochirality, dynamics and energy barriers, delivered by the combination of DFT and STM, provides insight on chirality transfer in heterogeneous catalysis (1-4).

(1) Dong, Y.; Goubert, G.; Groves, M. N.; Lemay, J.-C.; Hammer, B.; McBreen, P. H. *Acc. Chem. Res.* **2017**, DOI: 10.1021/acs.accounts.6b00516.

(2) Goubert, G.; Dong, Y.; Groves, M. N.; Lemay, J.-C.; Hammer, B.; McBreen, P. H. *Nat. Chem.* **2017**, DOI:10.1038/nchem.2753.

(3) Dong, Y.; Svane, K. L.; Lemay, J.-C., McBreen, P. H. *ACS Catal.* **2017**, *7*, 1757-1765.

(4) Goubert, G.; Demers-Carpentier, V.; Loach, R. P.; Lafleur-Lambert, R.; Lemay, J.-C.; Boukouvalas, J.; McBreen, P. H. *ACS Catal.* **2013**, *3*, 2677-2683.