Nonlinear Behaviour and the Limits of Mechanistic Understanding in Asymmetric Catalysis

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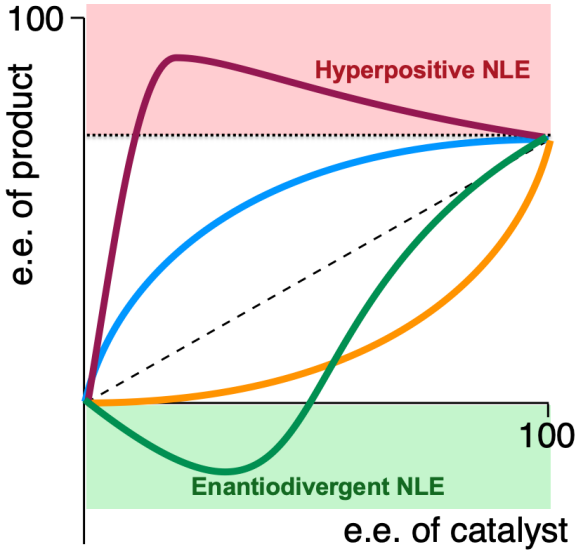
Asymmetric amplification is a phenomenon that plays a key role in the emergence of homochirality in life. In asymmetric catalysis, theoretical and experimental models have been investigated for understanding how chiral amplification is possible, in particular through non-linear effect.[1] Recently we have proposed models that have led to an understanding of more complex non-linear effects, such as hyperpositive and enantiodivergent non-linear effects, which include a coexistence of active monomeric and active dimeric species.[2,3] A higher degree of complexity seems attainable if one considers that higher levels of aggregation could be envisaged.[4]

We show here how different ligands, issued from the same privileged chiral structure, exhibit completely different systems-level behaviours and thus also different reaction outcomes – although they differ only by small chemical modifications. Mechanistic studies showed that the metal complexes aggregate and generate additional catalytic species in distinct ways. These results were obtained through a combination of nonlinear effect studies and other related studies and simulations have confirmed the possibility of such systems-level behaviour.

Overall, these results highlight the need to be cautious with certain paradigms of asymmetric catalysis, as structures alone do not necessarily predict systems-level behaviour that could bias the outcome of the catalytic reaction.



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