

## Matthieu Raynal



**Matthieu Raynal** got his PhD degree under the supervision of Dr P. Braunstein in 2009 (Strasbourg). He conducted postdoctoral studies at UPMC with L. Bouteiller (Paris) and in the group of Prof. P. W. N. M. van Leeuwen at ICIQ (Tarragona, Spain). In 2012, he was appointed as a CNRS researcher at Sorbonne Université, Paris (France), and obtained his Habilitation in 2018.

His group is currently developing supramolecular helical catalysts with particular efforts devoted to improve their chiral and switchable properties as well as improving known reactions or developing new ones. His research activities also concern the design of functional chiral assemblies and the structure–property relationship of chiral supramolecular polymers. The connection between the emergence of chirality in these systems and mechanism(s) leading to biological homochirality is also one of his points of interest. In a more general view, he is fascinated by how non-covalent interactions can be designed to control the outcome of a catalytic reaction, i.e. supramolecular catalysis. He recently co-edited with P. W. N. M. van Leeuwen the book “Supramolecular Catalysis: New Directions and Developments” (2022 Wiley-VCH GmbH). He was awarded the CNRS Bronze medal in 2017.

### Selected Publications:

- (1) “Switchable Supramolecular Helices for Asymmetric Stereodivergent Catalysis”, Chen, R.; Hammoud, A.; Aoun, P.; Martínez-Aguirre, M.; Vanthuyne, N.; Maruchenko, R.; Brocorens, P.; Bouteiller, L.; Raynal M., *Nature Commun.*, **2024**, *15*, 4116.
- (2) “Emergence of Homochiral Benzene-1,3,5-tricarboxamide Helical Assemblies and Catalysts upon Addition of an Achiral Monomer”, Li, Y.; Hamoud, A.; Bouteiller, L.; Raynal M., *J. Am. Chem. Soc.*, **2020**, *142*, 5676–5688.
- (3) “Dissecting the Role of the Sergeants in Supramolecular Helical Catalysts: From Chain Capping to Intercalation”, Martínez-Aguirre, M.; Li, Y.; Vanthuyne, N.; Bouteiller, L.; Raynal M., *Angew. Chem. Int. Ed.* **2021**, *60*, 4183–4191.
- (4) “Possible chemical and physical scenarios towards biological homochirality”, Sallembien, Q.; Bouteiller, L.; Crassous, J.; Raynal M., *Chem. Soc. Rev.*, **2022**, *51*, 3436-3476.

# Supramolecular helical catalysts: chirality induction and beyond

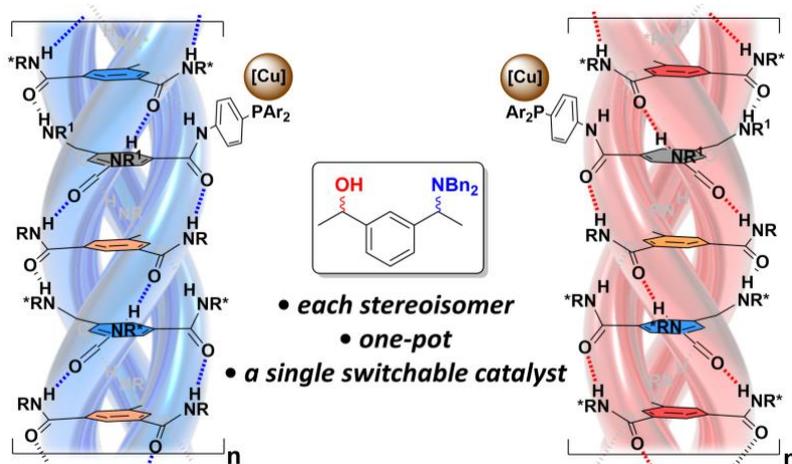
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Helices are commonly formed by symmetry breaking operating during the bottom-up assembly of small molecules or monomers and their sense of rotation can be controlled by various methods. Important progress has been made in controlling the chiral and structural properties of supramolecular discrete assemblies and polymers.<sup>[1]</sup> Benzene-1,3,5-tricarboxamide<sup>[2]</sup> (BTA) are ubiquitous synthons for the preparation of hydrogen-bonded helices but it remains to be demonstrated how a given macroscopic property, notably related to chirality (e.g. chiroptical, magnetic, catalytic), can be affected by tuning the structure of these supramolecular polymers or copolymers. We demonstrated that the supramolecular chirality of BTA assemblies can be transferred to intrinsically achiral metal centres (Rh, Cu) located at their periphery.<sup>[3]</sup> How the selectivity of a catalytic reaction of reference can be affected by the nature of the monomers, the presence of metal centres, and the addition of achiral additives will be particularly discussed.<sup>[4]</sup> Not only a fine tuning of the chirality of the supramolecular assemblies but also a proper control of their dynamicity is key to address important challenges. We recently disclose the possibility to select one major (70%-79%) amongst four possible stereoisomers of an amino alcohol by applying the supramolecular helical catalyst in either concomitant (with no inversion of catalyst handedness) or sequential (with inversion of catalyst handedness) hydrosilylation and hydroamination reactions (Figure).<sup>[5]</sup>



**Figure.** Supramolecular helical catalysts used in a stereodivergent asymmetric process.

## References

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- [2] Cantekin S. et al. *Chem. Soc. Rev.*, **2012**, *41*, 6125.
- [3] Desmarchelier A. et al. *J. Am. Chem. Soc.*, **2016**, *138*, 4908.
- [4] (a) Li Y. et al. *J. Am. Chem. Soc.*, **2020**, *142*, 5676. (b) Martínez-Aguirre M. A. et al. *Angew. Chem. Int. Ed.*, **2021**, *60*, 4183. (c) Hammoud A. et al. *Chem. Eur. J.*, **2023**, e202300189. (d) Kong H. et al. *ChemistryEurope*, **2023**, *1*, e202300027.
- [5] Chen, R. et al. *Nature Commun.*, **2024**, *15*, 4116.