



**HAL**  
open science

## Schiff base helicenes

Nicolas Zigon, Mariia Savchuk, Steven Vertueux, N. Avarvari

► **To cite this version:**

Nicolas Zigon, Mariia Savchuk, Steven Vertueux, N. Avarvari. Schiff base helicenes. ISCOM2019, Sep 2019, Tomar, Portugal. 2019. hal-02889192

**HAL Id: hal-02889192**

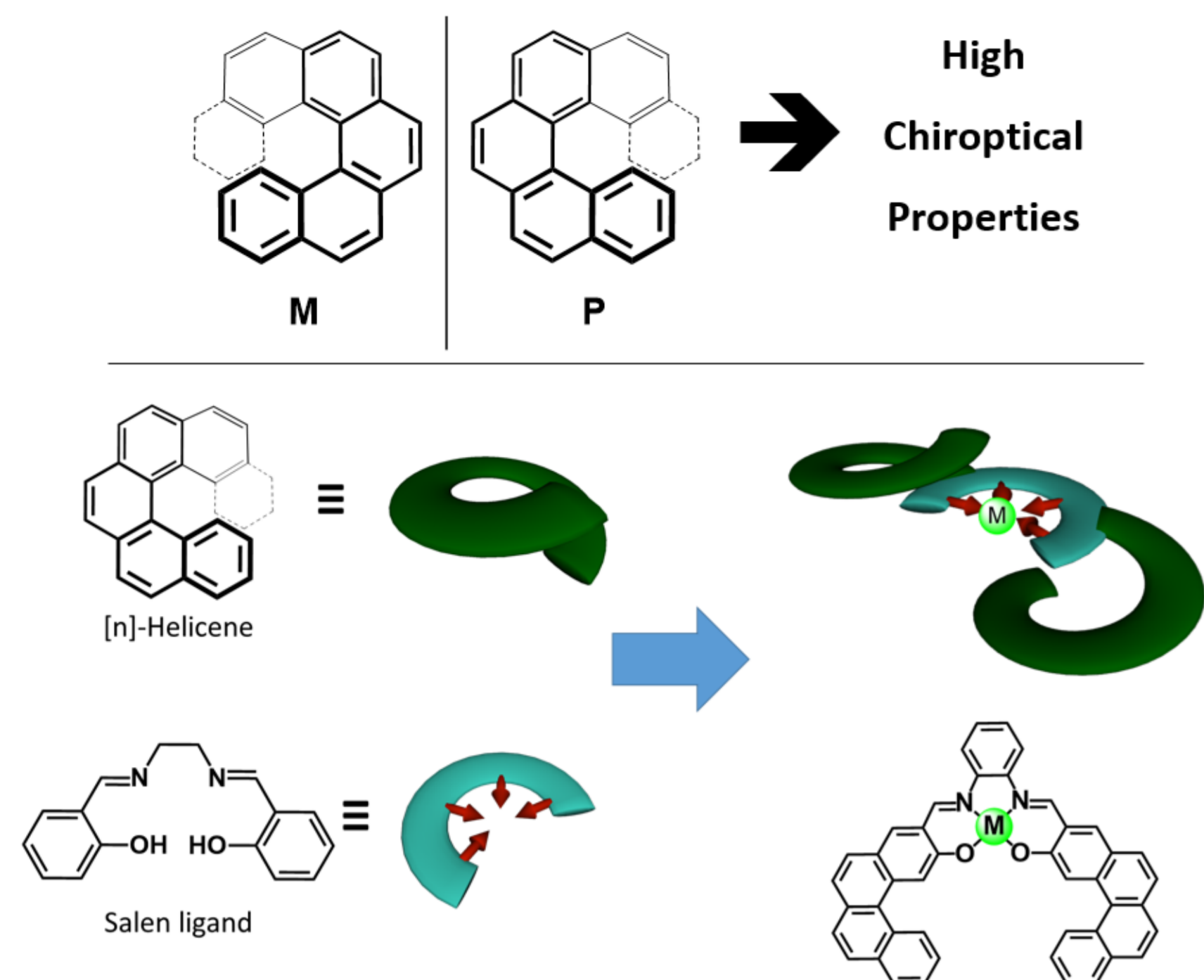
**<https://hal.science/hal-02889192v1>**

Submitted on 3 Jul 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Nicolas Zigon, Mariia Savchuk, Steven Vertueux, and Narcis Avarvari  
Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 49045 Angers Cedex, France  
nicolas.zigon@univ-angers.fr



## Goals

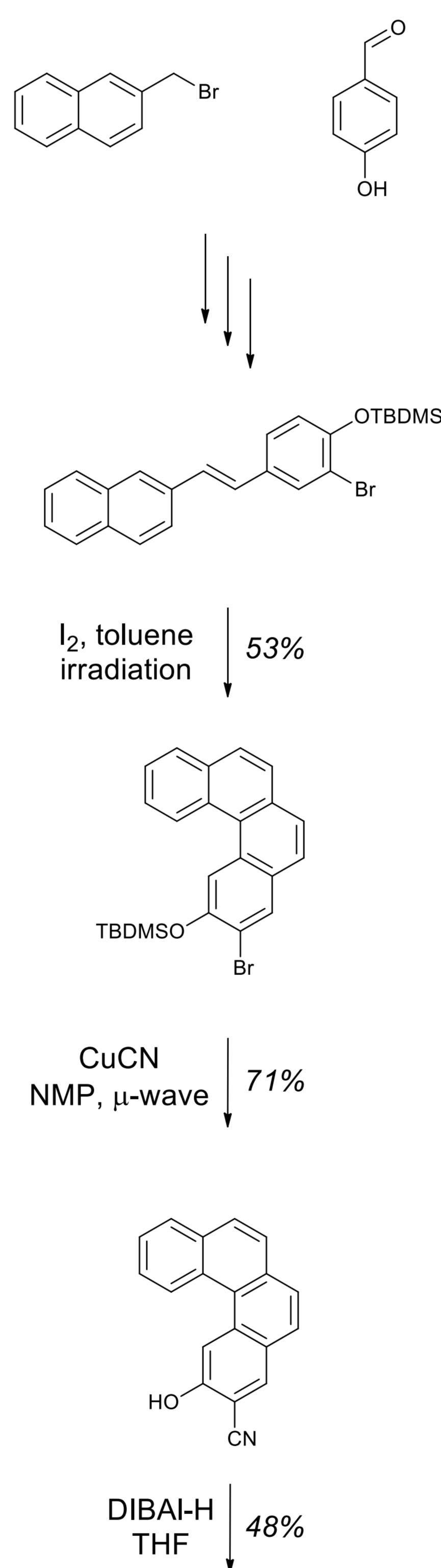
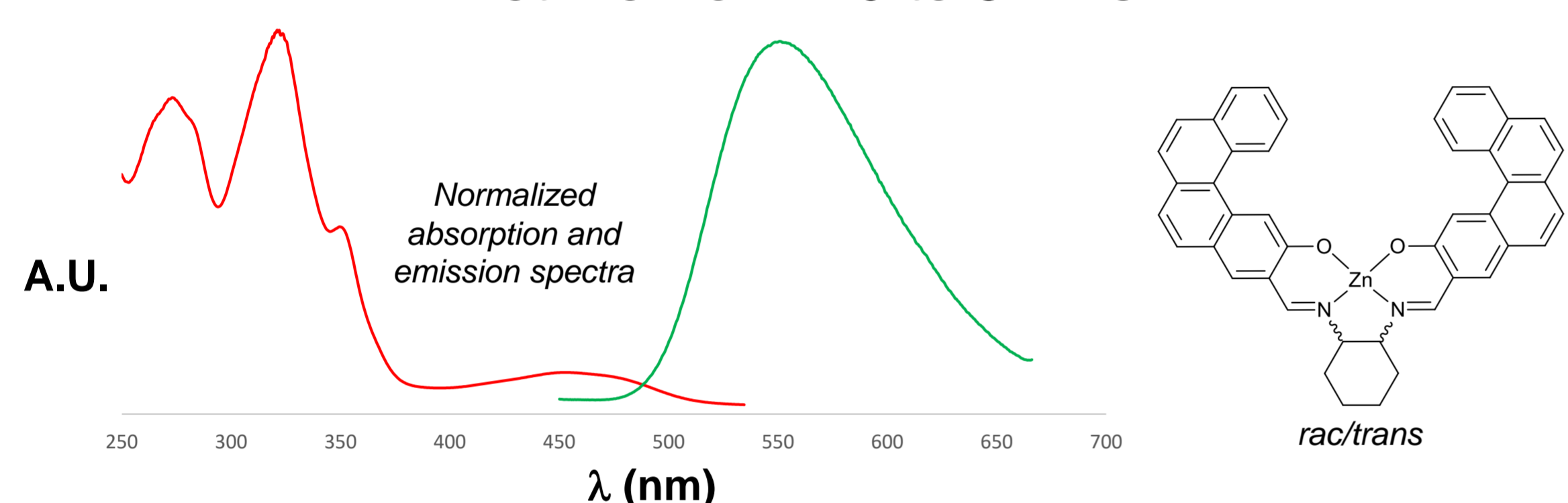
Circularly polarized light emitters or complexes displaying magnetochiral dichroism (linking magnetism and chirality) are actively researched species.<sup>1</sup> Helicenes form a class of chiral molecules renowned for their intriguing physical properties, particularly their typical helicoidal structure and exceptional chiroptical properties (intense optical activity and circular dichroism). On the other hand, salen ligands are chelating tetradentate Schiff bases whose complexes with metals possess excellent properties in catalysis, luminescence or magnetism, for example.<sup>2</sup> The controlled synthesis of chiral magnets as complexes containing both helicene and salen moieties is therefore an important challenge.<sup>3</sup> A consistent and systematic study for the synthesis of helicene/salen based derivatives was therefore designed in our group, in order to access compounds displaying magnetochiral dichroism.

## Synthetic methods and characterizations

A synthetic pathway based on a Wittig reaction between a phosphonium ylide and a functionalized aldehyde, followed by a photocyclisation in diluted conditions yields a brominated [4]helicene, whose substitution by cyanide and subsequent reduction to the aldehyde afford the Schiff base precursor. Reaction with 0.5 equivalent of diamine in MeOH in the presence of a metal provides the desired complexes in good yields (80-90%) for the last step.

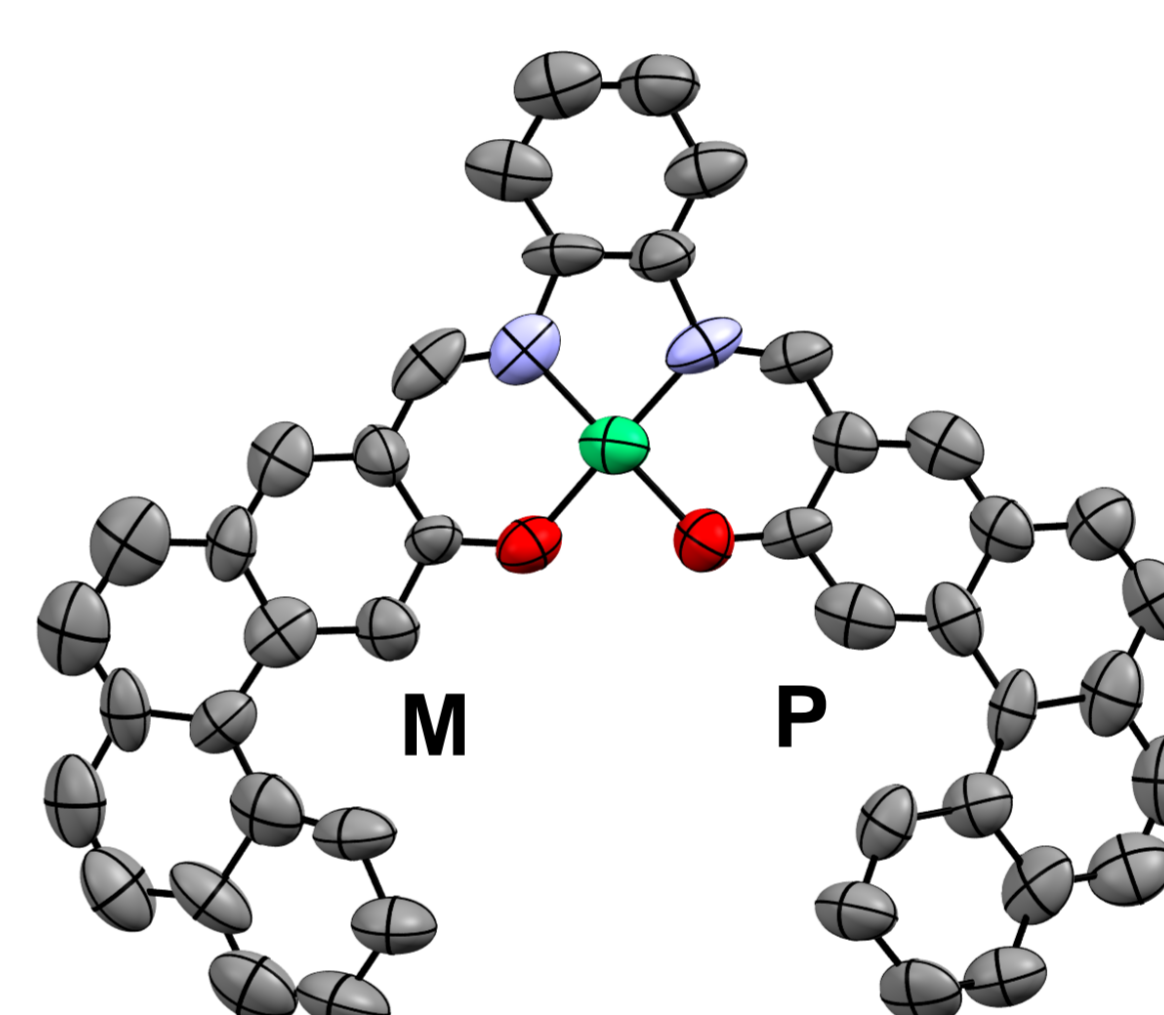
### Luminescence properties

Yellow emission  
Quantum yields from 3 to 16%  
Lifetime from 1.0 to 5.4 ns



### X-Ray structure

Structure of the Ni-complex crystallized in P<sub>2</sub><sub>1</sub>/c space group.

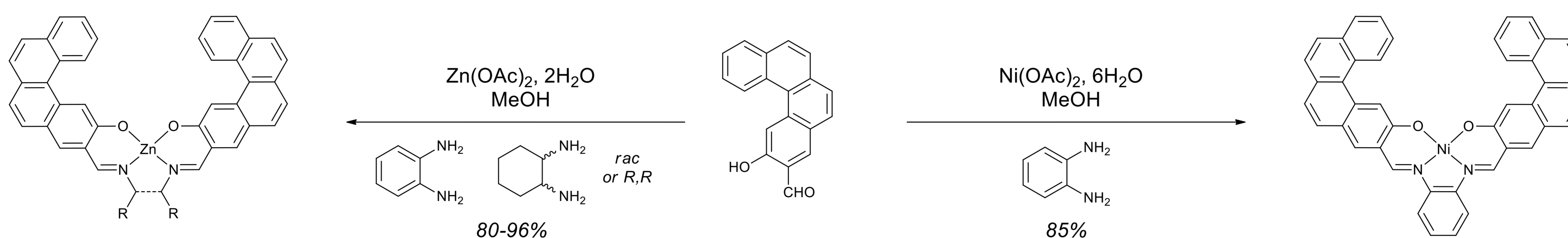
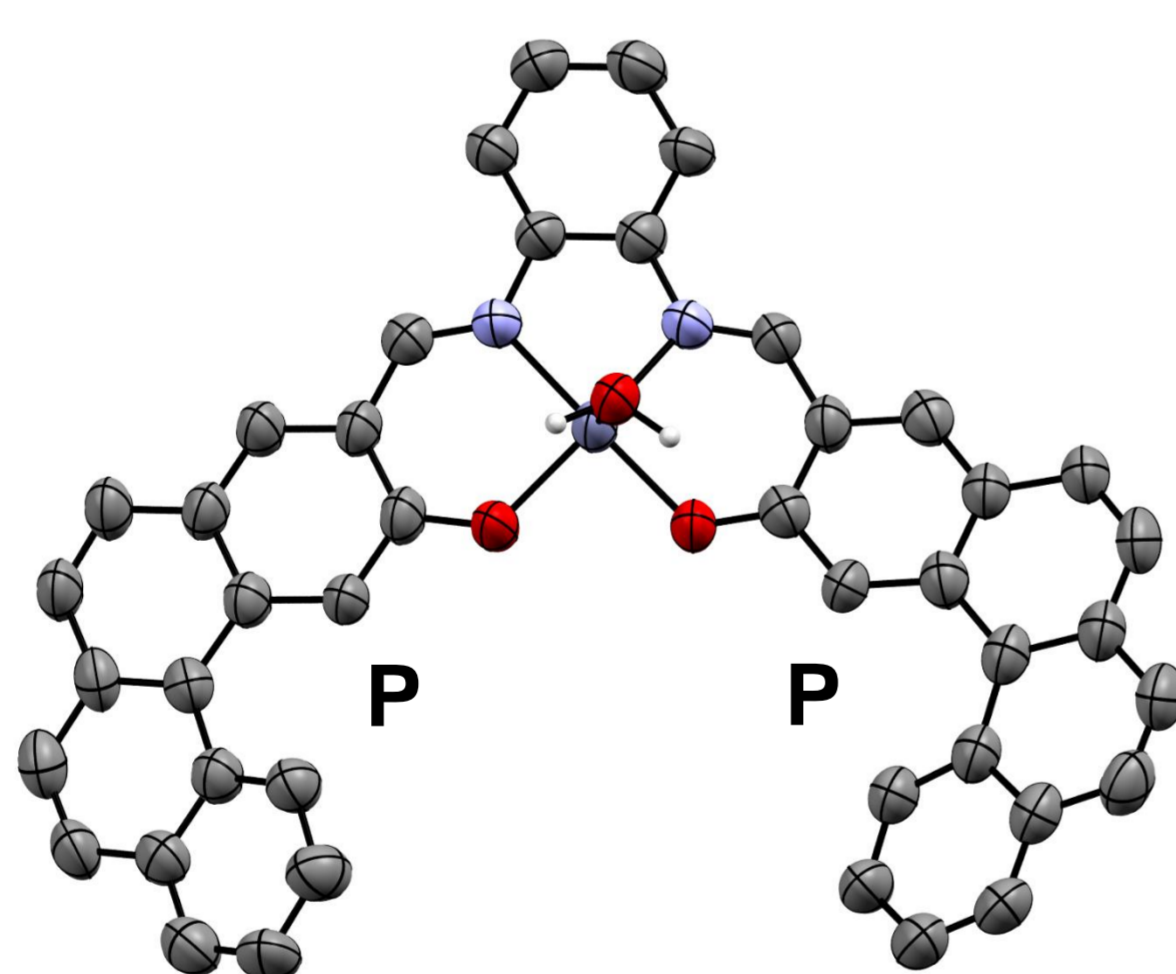


Formula	C <sub>44</sub> H <sub>26</sub> N <sub>2</sub> NiO <sub>2</sub> 2,5-(CH <sub>3</sub> OH)
Crystal system	Monoclinic
Space group	P <sub>2</sub> <sub>1</sub> /c
R <sub>1</sub>	0.1259
wR <sub>2</sub>	0.2829
GoF	0.965

### X-Ray structure

Structure of the Zn-complex crystallized in P<sub>2</sub><sub>1</sub>/c space group

Formula	C <sub>44</sub> H <sub>28</sub> N <sub>2</sub> ZnO <sub>3</sub> ·(THF)
Crystal system	Monoclinic
Space group	P <sub>2</sub> <sub>1</sub> /c
R <sub>1</sub>	0.0941
wR <sub>2</sub>	0.2259
GoF	1.035



## Perspectives

A robust synthetic pathway was designed for the synthesis of Schiff base helicenes. Nevertheless, the inherent flexibility of [4]helicene denies it any chirality at room temperature. The synthesis of Schiff base [6]helicene coupled to chiral resolution will provide chiral and conformationally stable complexes. CD and CPL spectra will be recorded for the complexes, and magnetic optical properties will be measured. Thanks to the versatility of the organic platform, the extension of this strategy to other metals with magnetic (e.g. Cu<sup>II</sup>) or catalytic properties (e.g. Mn<sup>III</sup>) will be straightforward.

## Bibliography

1. a) Wagnière G., Meier A. *Chem. Phys. Lett.*, **1982**, 93(1), 78–81 ; b) Biet T., Cauchy T., Sun Q., Ding J., Hauser A., Oulevey P., Burgi T., Jacquemin D., Vanthuyne N., Crassous J., Avarvari N., *Chem. Commun.* **2017**, 53, 9210–9213 ; c) Y. Shen, C.-F. Chen, *Chem. Rev.* **2012**, 112, 1463–1535 ; d) M. Gingras, *Chem. Soc. Rev.* **2013**, 42, 1051–1095. e) Pop F., Zigon N., Avarvari N., *Chem. Rev.*, **2019**, 119, 8435–8478.
2. a) Cozzi P. G. *Chem. Soc. Rev.*, **2004**, 33(7), 410–421 ; b) Sammis G. M., Danjo H., Jacobsen E. N. *J. Am. Chem. Soc.*, **2004**, 126(32), 9928–9929 ; c) Yoon T. P. *Science*, **2003**, 299(5613), 1691–1693 ; d) Whiteoak C. J., Salassa G., Kleij A. W. *Chem. Soc. Rev.*, **2012**, 41(2), 622–631 ; e) Nassief A. R., Abdel-Hafiez M., Hassen A., Khalil A. S. G., Saber M. R. *J. Magn. Magn. Mater.*, **2018**, 452, 488–494.
3. a) Train C., Gheorghie R., Krstic V., Chamoreau L.-M., Ovanesyan N. S., Rikken G. L. J. A., Gruselle M., Verdaguer M., *Nat. Mater.*, **2008**, 7, 729–734 ; b) Kim S., Kim J., Shin D., Kim Y., Ha Y., *Bull. Korean Chem. Soc.* **2001**, 22, 743–747 ; c) Yu T., Su W., Li W., Hong Z., Hua R., Li B. *Thin Solid Films*, **2007**, 4080–4084 ; d) Barwiolek M., Szlyk E., Muzioła T. M., Lis T., *Dalton Trans.*, **2011**, 40, 11012–11022.