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Schiff base helicenes

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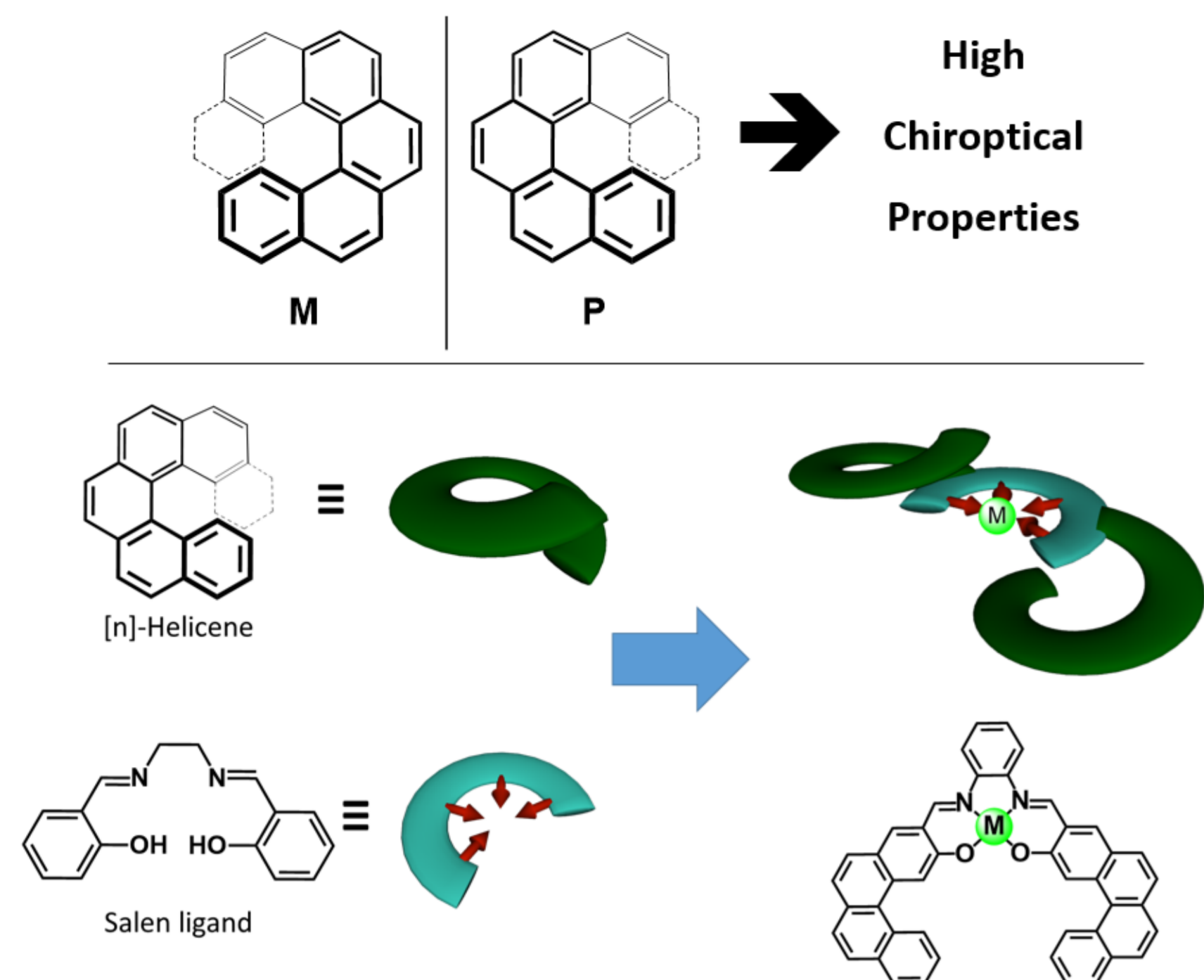
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Goals

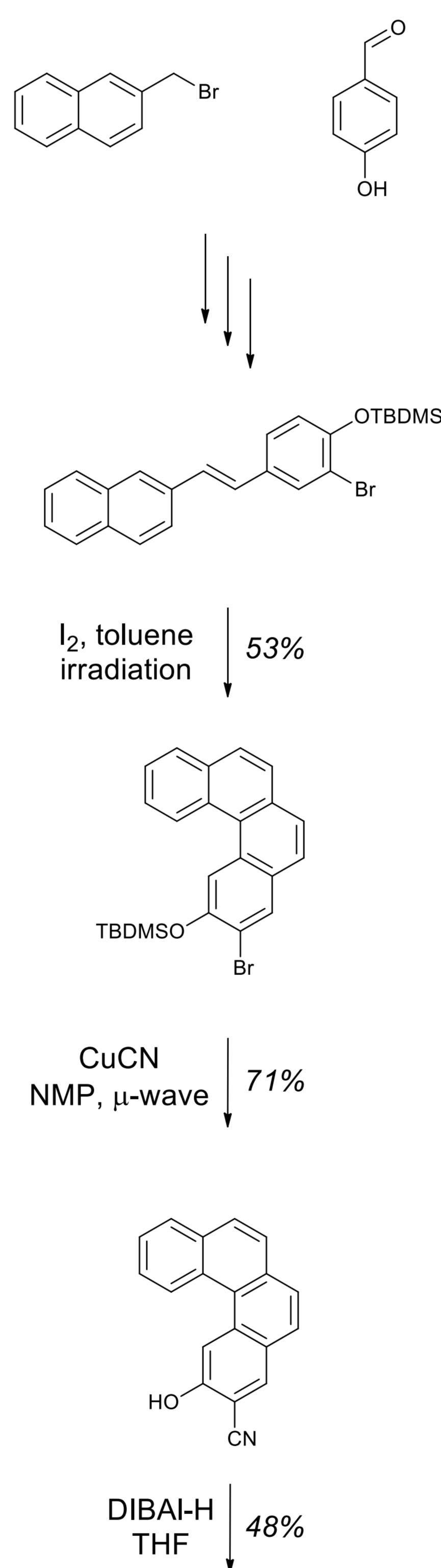
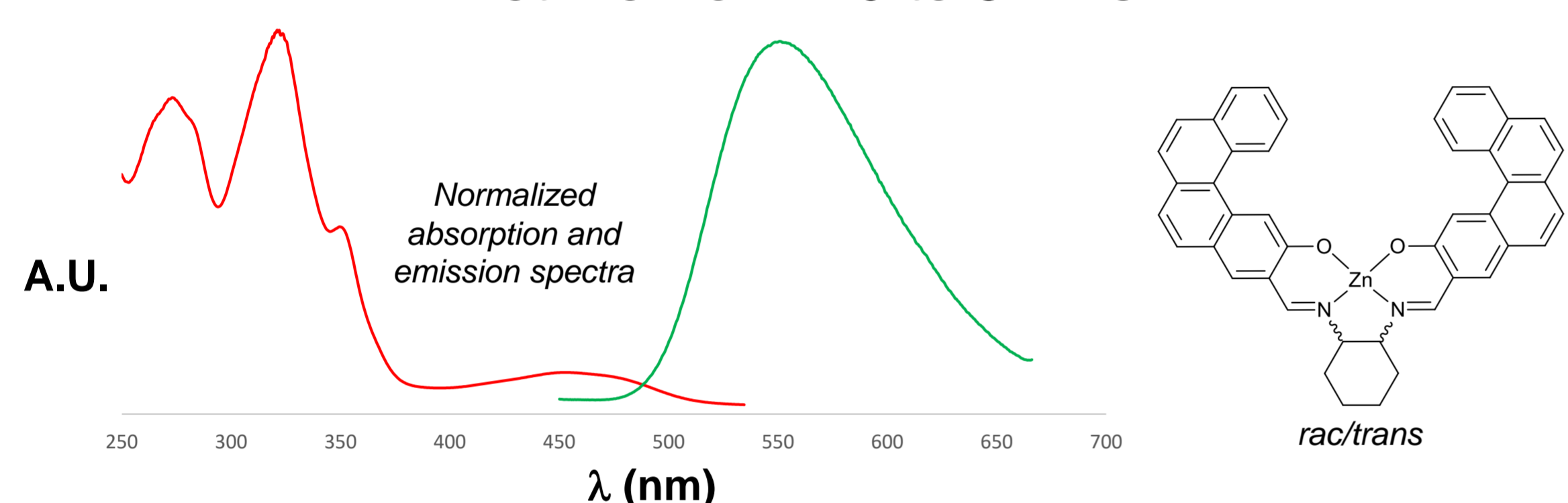
Circularly polarized light emitters or complexes displaying magnetochiral dichroism (linking magnetism and chirality) are actively researched species.¹ Helicenes form a class of chiral molecules renowned for their intriguing physical properties, particularly their typical helicoidal structure and exceptional 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.² The controlled synthesis of chiral magnets as complexes containing both helicene and salen moieties is therefore an important challenge.³ 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.

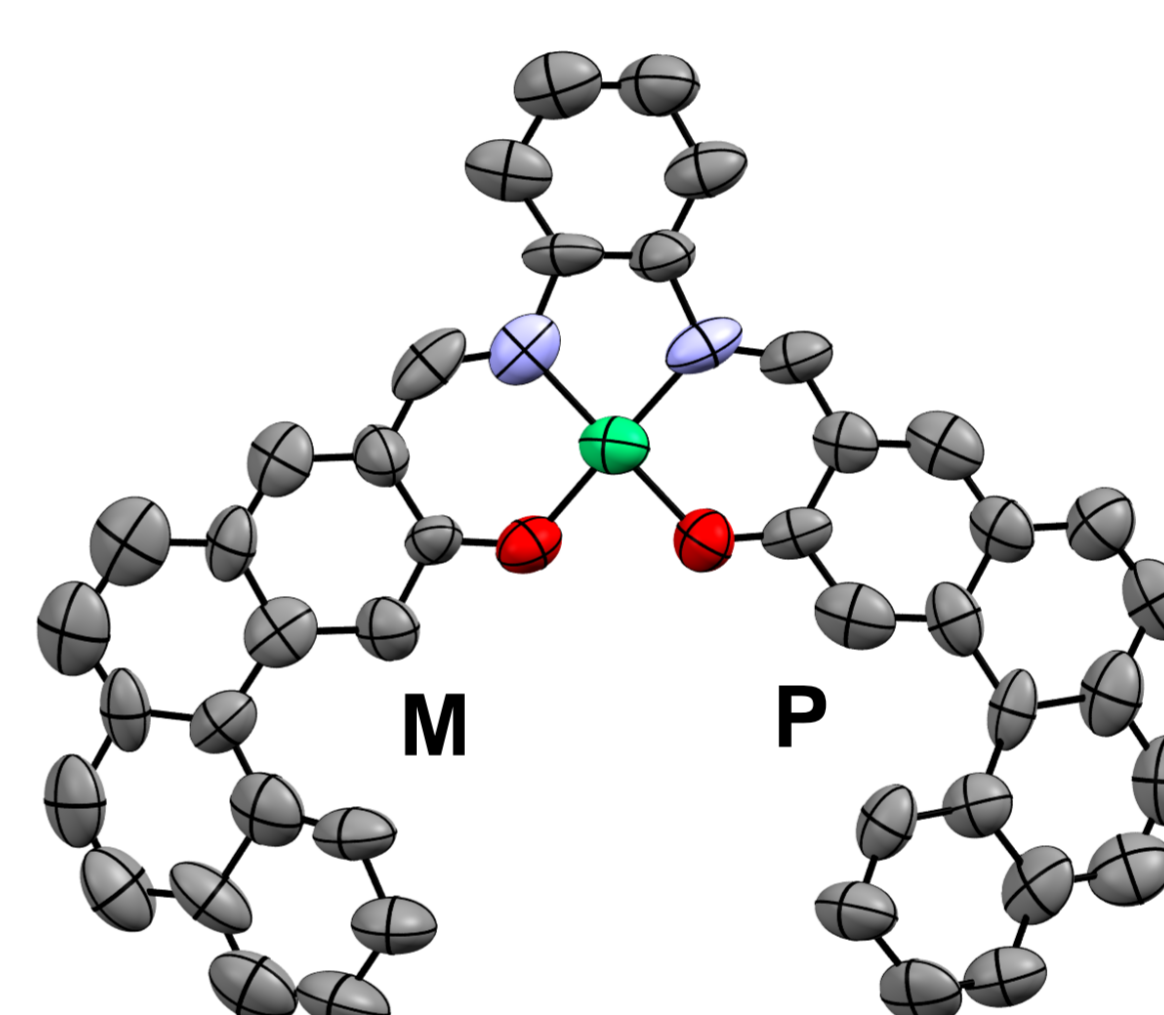
Luminescence properties

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 $P2_1/c$ space group.

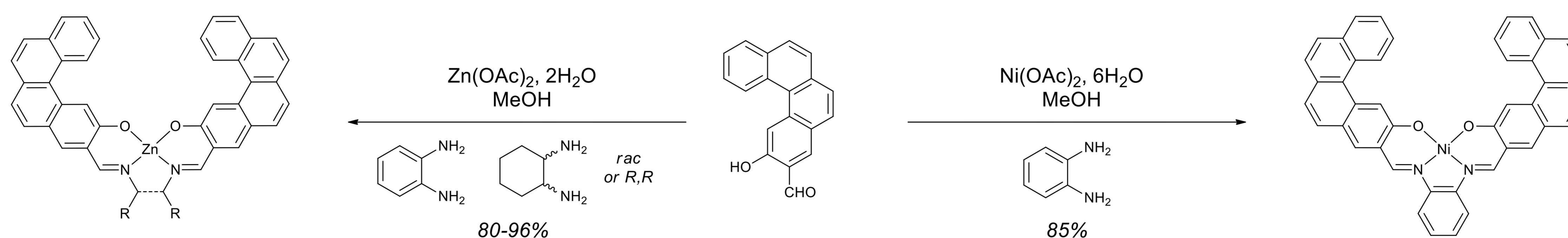
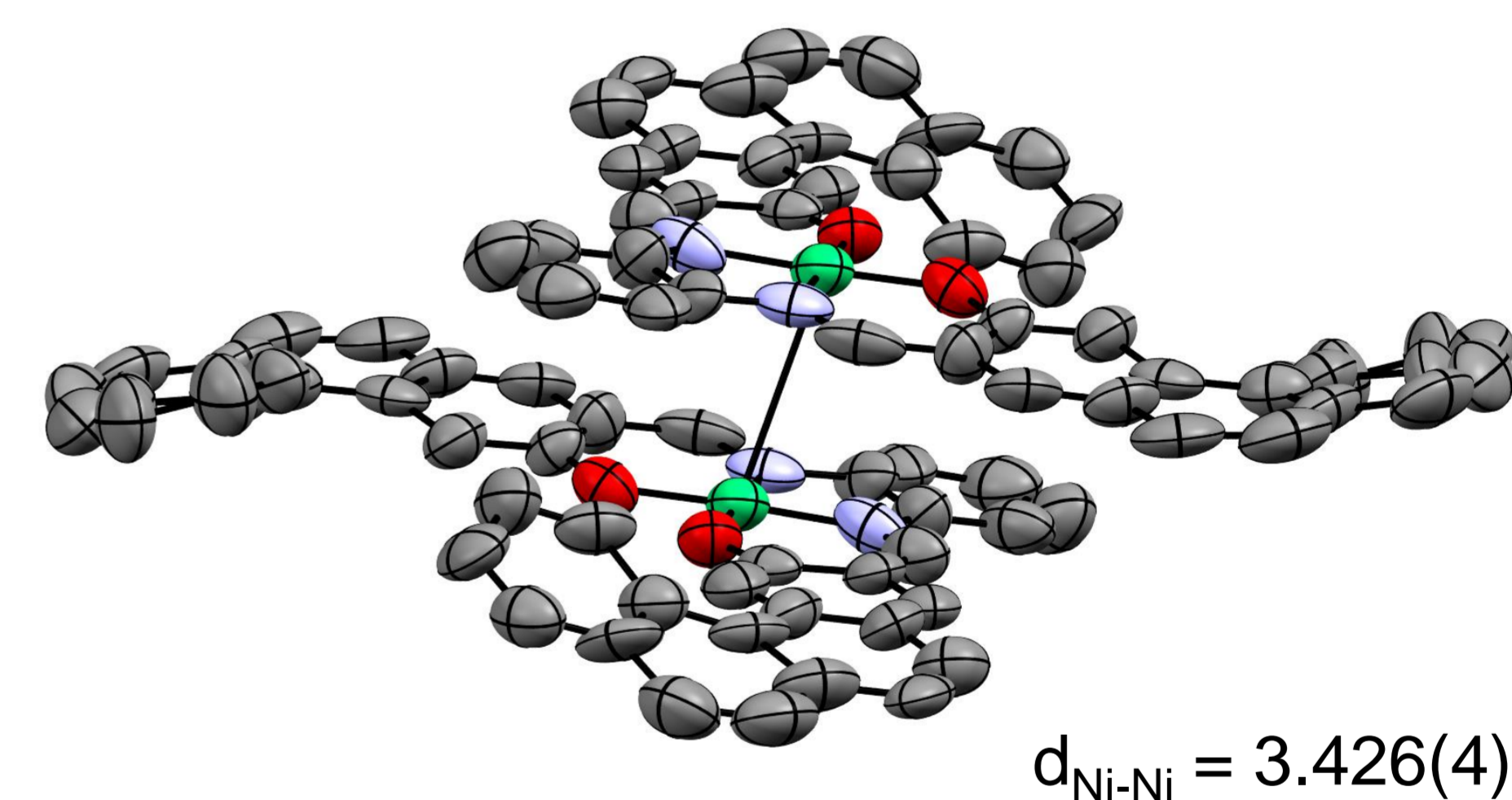
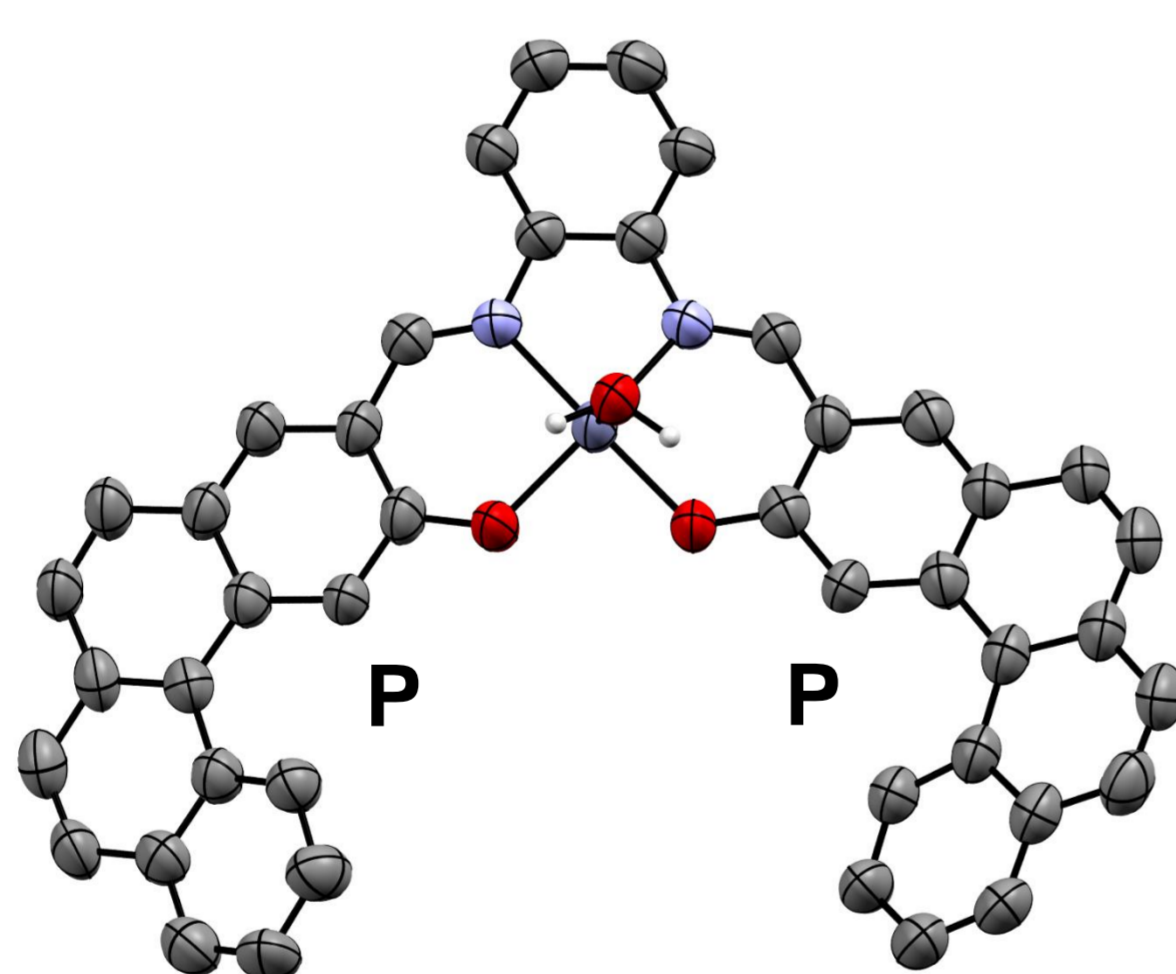


Formula	$C_{44}H_{26}N_2NiO_2$ $2,5-(CH_3OH)$
Crystal system	Monoclinic
Space group	$P2_1/c$
R_1	0.1259
wR_2	0.2829
GoF	0.965

X-Ray structure

Structure of the Zn-complex crystallized in $P2_1/c$ space group

Formula	$C_{44}H_{28}N_2ZnO_3$ $\cdot(THF)$
Crystal system	Monoclinic
Space group	$P2_1/c$
R_1	0.0941
wR_2	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^{II}) or catalytic properties (e.g. Mn^{III}) will be straightforward.

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