

DNA-Based Asymmetric Photocatalysis



Zachary PASTOREL^a, Juliette ZANZI^b, Stellios ARSENIYADIS^c, Yves CANAC^b, Olivier BASLE^b, and Michael SMIETANA^a

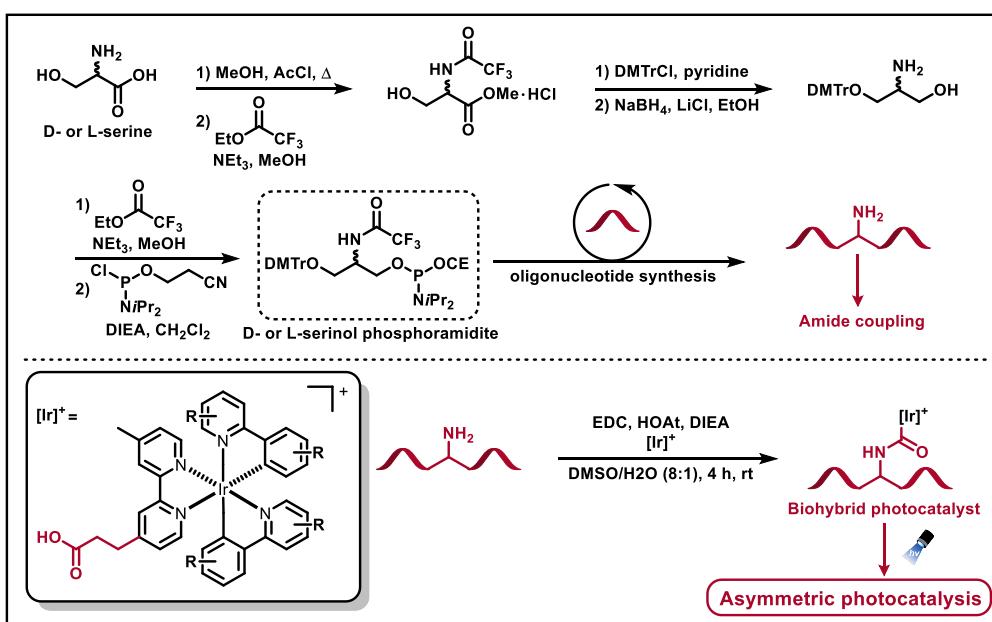
^a Institut des Biomolécules Max Mousseron, équipe ChemBioNAC, Université de Montpellier, CNRS, ENSCM Montpellier, France

^b Laboratoire de Chimie de Coordination, Université Paul Sabatier, Toulouse, France

^c Queen Mary University of London, Department of Chemistry, London E1 4NS, United Kingdom

Chirality is a crucial factor in molecular recognition processes observed in biological systems. While chemists have developed a large variety of chiral ligands able to generate enantiopure compounds, asymmetric biocatalysis, relying on stereoselective, energy-efficient, and environmentally friendly processes, has witnessed significant advancements in recent years.¹ In this context, our group has been dedicated to develop a series of highly enantioselective transformations that rely on the transfer of chirality from the DNA double helix.² This approach is based on the covalent or non-covalent anchoring of an achiral Cu(II) bipyridine ligand into natural or modified DNA.³ More recently, the ligand was covalently anchored into an oligonucleotide through the synthesis of a serinol phosphoramidite synthon which, after being incorporated, was coupled via an amide link to bipyridines (Scheme).

Similarly, drawing inspiration from natural photosynthesis, photocatalyzed reactions have experienced rapid growth and have found application in various chemical transformations.⁴ In continuation of our work, we decided to embark in the synthesis of modified DNA functionalized with Ir(III) photocatalyst. This was achieved by reacting our serinol-modified oligonucleotide with acid-modified photocatalysts. We will present the synthesis of this new hybrid photocatalyst and its applications in enantioselective photocatalysis (Scheme).



References

- ¹ a) Roelfes, G.; Feringa, B. L. *Angew. Chem. Int. Ed.* **2005**, *44*, 3230. b) Boersma, A. J.; Feringa, B. L.; Roelfes, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 3346.
- ² a) Wang, J.; Benedetti, E.; Bethge, L.; Vonhoff, S.; Klussmann, S.; Vasseur, J.-J.; Cossy, J.; Smietana, M.; Arseniyadis, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 11546. b) Benedetti, E.; Duchemin, N.; Bethge, L.; Vonhoff, S.; Klussmann, S.; Vasseur, J.-J.; Cossy, J.; Smietana, M.; Arseniyadis, S. *Chem. Commun.* **2015**, *51*, 6076. c) Duchemin, N.; Skiredj, A.; Mansot, J.; Leblanc, K.; Vasseur, J.-J.; Beniddir, M. A.; Evanno, L.; Poupon, E.; Smietana, M.; Arseniyadis, S. *Angew. Chem. Int. Ed.* **2018**, *57*, 11786.
- ³ Duchemin, N.; Aubert, S.; de Souza, J. V.; Bethge, L.; Vonhoff, S.; Bronowska, A. K.; Smietana, M.; Arseniyadis, S. *JACS Au* **2022**, *2*, 1910.
- ⁴ a) Yoon, T. P. *Acc. Chem. Res.* **2016**, *49*, 2307. b) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, *116*, 10035. c) Zhang, L.; Meggers, E. *Acc. Chem. Res.* **2017**, *50*, 320.