# Macrocyclic ligands giving access to robust photosensitizers based on copper complexes

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## PhD thesis project

A recent study conducted by our two teams has shown that macrocyclic ligands containing a coordinating unit of the diphosphine or diimine type can be used to stabilize $[Cu(NN)(PP)]^+$ complexes in solution and enhance their luminescent properties.[1] We now aim at developing even more efficient copper complexes that exhibit redox reversibility between the +I and +II oxidation states of copper. To achieve this, cyclodextrin-based macrocyclic diphosphines will be combined with macrocyclic diimines (bpy, phen, etc.) or triimine (tpy) within a mechanically interlocked molecule of the catenate or rotaxane type, which should prevent any ligand exchange reactions regardless of the metal's oxidation state. Such a molecular architecture has the potential to further increase the stability of the targeted complexes and enhance their photophysical properties. The design of highly robust photosensitizers based on these principles should ultimately open up new perspectives in photocatalysis, as it will avoid the use of complexes based on environmentally harmful and expensive second- and third-row transition metals.[32]

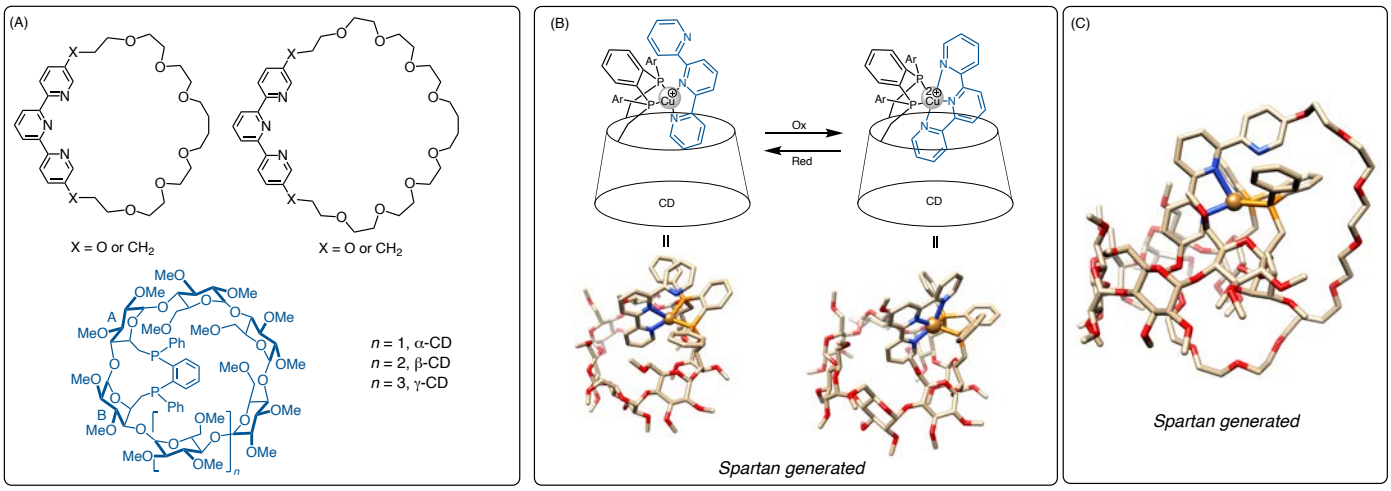


**Figure 1**. A) Macrocyclic nitrogen and phosphorus ligands; B) copper(I)/(II) complexes comprising an encapsulated tpy ligand; C) $[Cu(NN)(PP)]^+$ catenate comprising a cavity-shaped diphosphine mechanically interlocked by a macrocyclic tpy ligand.

*The objective of this thesis funded by the ANR (French Research Council) will be to prepare new heteroleptic copper(I) complexes containing a diimine or triimine ligand and a metal-confining diphosphine based on cyclodextrins (CDs) in order to study their electrochemical and photophysical properties and test them for their ability to act as efficient and robust sensitizers in photocatalytic reactions. The fields of chemistry addressed in this project will include organic synthesis, supramolecular chemistry, coordination chemistry, photochemistry and homogeneous catalysis. Interest in these five areas, as well as some previous experience in molecular chemistry, are highly desirable.*

*To apply, please send your CV along with your master transcripts (1st and 2nd year) to d.armspach@unistra.fr. Only candidates having an overall average of at least 60% at their master's degree will be considered.*

*Website: http://armspach.com*

[1] T. A. Phan, N. Armaroli, A. S. Moncada, E. Bandini, B. Delavaux-Nicot, J. F. Nierengarten, D. Armspach, *Angew. Chem. Int. Ed.* **2023**, *62*, e202214638.
[2] J. Beaudelot, S. Oger, S. Perusko, T. A. Phan, T. Teunens, C. Moucheron, G. Evano, *Chem. Rev.* **2022**, *122*, 16365-16609.