[Project supported by FrenchBIC] The selectivity and catalytic activities of site-specific pyrene-modified laccase on carbon nanotube electrodes

Yunfei Dang, from the Roessler group at Imperial College London, spent one week in the Bioscience group, iSm2 (Institute of Science Molecular De Marseille). This project was supported by a grant from FrenchBIC.

My PhD project aims to establish a novel platform for film-electrochemical electron paramagnetic resonance spectroscopy (FE-EPR) using carbon nanotube electrodes. FE-EPR makes it possible to track the evolution of radical intermediates during electrocatalysis. Thus, FE-EPR enables active-site states to be observed during catalysis. Initially focusing on small organic radicals as electrocatalysts, I am now expanding the capability of FE-EPR to biological catalysts. Fungal laccase, a type of multicopper oxidase that possesses a near-surface mononuclear copper centre (T1) and an embedded trinuclear copper centre (TNC), can reduce dioxygen to water. However, direct detection of key paramagnetic intermediates at these centres during enzyme catalysis is lacking.

The Bioscience group has successfully demonstrated efficient direct electron transfer between the electrode surface and the T1 and TNC centres, and their selective catalytic activities using site-specifically modified laccases. This method can be transferred to my FE-EPR platform to enable further mechanistic investigations into those copper centres during dioxygen reduction.

As a first step, it is important to achieve effective loading of enzyme for electrochemical catalysis. Therefore, I spent one week with Dr. Alexandre Ciaccafava in the Bioscience group at iSm2, who has an extensive expertise in laccase modification and catalytic studies. Initially, I experimented with multiple methods to maximize enzyme loading on my carbon nanotube electrodes. Then, various engineered enzymes with immobilization sites closer to either the T1 or TNC were loaded and tested for catalytic activities. The results are promising, showing the expected dependency between activity and orientation of the laccase. We will continue this collaboration to further study the paramagnetic intermediates of laccase using our FE-EPR methodology.

I would like to acknowledge FrenchBIC for the grant and the Bioscience group for the opportunity to work in their lab. It was a great week of experiments and scientific discussions.