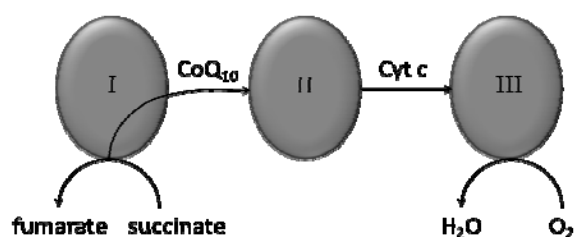


## Effects of Axial Ligation and Electron Donors on Oxygen Reduction Catalysis by Metalloporphyrins.

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Oxygen reduction is a part of numerous biological cycles. As opposed to heterogeneous oxygen reduction catalysis in man created devices, *e.g.*, fuel cells, enzymatic catalysis of the reaction at ambient temperatures is very effective<sup>1</sup> and markedly outperforms the heterogeneous catalysis in terms of active site turnover frequency. As metalloporphyrins are frequently the catalytic sites for oxygen reduction in the biological cycles, numerous attempts have been made to develop heterogeneous oxygen reduction catalysts utilizing iron or cobalt porphyrins.<sup>2</sup> None of such attempts resulted in catalytic activities that could compete with those observed in enzymatic catalysis, most likely because the active site was deprived of other essential components participating in the enzymatic processes. For example, in the citric acid cycle, oxygen is reduced by cytochrome c oxidase in which the catalytic center is a metallo-porphyrin axially coordinated by an imidazole derivative (His376). Electrons required for oxygen reduction are shuttled to the catalytic center by red-ox active molecules such as ubiquinone (coenzyme Q<sub>10</sub>, CoQ<sub>10</sub>) that undergo a series of fast electron transfers (Fig. 1).



**Figure 1.** A simplified mechanism of oxygen reduction in the Krebs cycle (citric acid cycle).

In our talk we will present the results of our study on the effects of axial coordination and red-ox coupling with various electron donors on the catalytic activity of selected metalloporphyrins for oxygen reduction under electrochemical conditions.

### Acknowledgements

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### References

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