Mechanistic insights into (bio)catalysts from unpaired electrons

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Unpaired electrons play an important role in numerous redox-driven catalytic processes. Controlling their location and exploiting the interactions with their environment can provide key mechanistic information into these catalytic reactions. In this talk I will discuss how we are exploiting and developing EPR-based techniques in conjunction with biochemistry, electrochemistry and materials chemistry to gain mechanistic insights into metalloenzymes[1] and electron-transfer based catalytic reactions more generally.

I will showcase how we have used pulse EPR to understand the proton-coupled electron transfer mechanism in respiratory complex I.[2,3] I will then introduce film-electrochemical EPR spectroscopy (FE-EPR) as a new tool to investigate surface-bound molecular catalysts. With *operando* FE-EPR we can monitor the evolution of radicals during catalysis in real time.[4] I will further discuss our ongoing work on extending FE-EPR to metalloenzymes,[5] on being able to probe faster timescales, and on exploring different electrode materials for applicability to diverse catalysts.

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3 E. Clifford, J. J. Wright, A. Collauto, J. Hirst and M. M. Roessler, *doi.org/10.26434/chemrxiv-2025-br3z5*.

4 M. Seif-Eddine, S. J. Cobb, Y. Dang, K. Abdiaziz, M. A. Bajada, E. Reisner and M. M. Roessler, *Nature Chemistry 2024 16:6*, 2024, **16**, 1015–1023.

5 D. Facchetti, Y. Dang, M. Seif-Eddine, B. L. Geoghegan and M. M. Roessler, *Chemical Communications*, 2024, **60**, 12690–12693.