

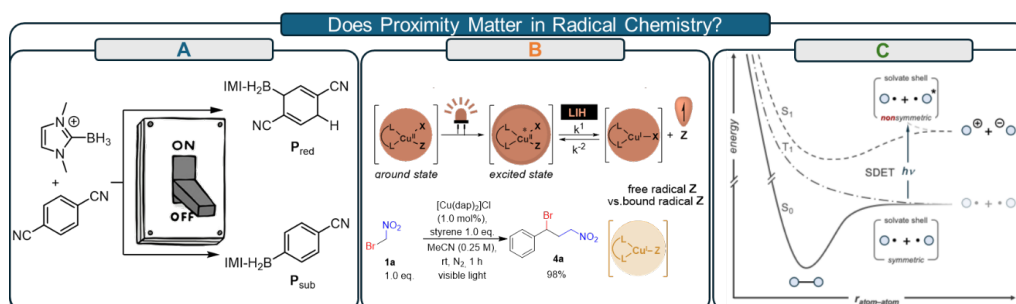
## Radicals Pairs – Impact on Radical Reactivity

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Radical intermediates are central in many transformations, particularly those initiated by light or occurring under photocatalytic conditions. A fundamental challenge is controlling their reactivity in bimolecular transformations in solution. If modifying the radical itself is not an option, usually its concentration in solution must be carefully regulated to achieve the desired selectivity.



In this contribution, we discuss our latest findings on how more proximity effects can modulate radical reactivity. The first study explores what governs chemoselectivity in the photocatalytic reaction of electron-poor arenes with Lewis acid-base adducts of N-heterocyclic carbenes and boranes (Figure A).[1] The second highlights copper photoredox catalysis, demonstrating how copper cleverly influences radical reactivity by inner-sphere pathways (Figure B).[2] The third, seemingly unrelated to proximity control, investigates the transformation of radicals into ion pairs via a two-stimuli activation of homopolar bonds (stimulated doublet electron transfer, SDET, Figure C). Yet, proximity within the resulting radical pairs appears crucial to success. This study not only has broad implications for synthetic chemistry but also raises intriguing mechanistic questions about the conditions required for effective SDET.[3] Our mechanistic investigations integrate computational chemistry, transient absorption spectroscopy, and magnetic resonance techniques (EPR, CIDNP-NMR).

[1] Two manuscripts in preparation, citations will be made available in the talk.

[2] a) A. Reichle, M. Koch, H. Sterzel, L.-J. Großkopf, J. Floss, J. Rehbein\*, O. Reiser\* *Angew. Chem. Int. Ed.*, **2023**, e202219086; b) A. Reichle, H. Sterzel, P. Kreitmeier, R. Fayad, F. N. Castellano\*, J. Rehbein\*, O. Reiser *Chem. Commun.*, **2022**, 58, 4456-4459.

[3] Tiefel, A.F., Grenda, D.J., Allacher, C. Hernández-Castillo, P. R. Narasimhamurthy, K. Zeitler, L. González, Julia Rehbein\*, P. Nuernberger\*, A. Breder\* *Nature* **2024**, 632, 550–556.Text:

### Short CV:



Julia Rehbein studied chemistry at the TU Dresden (2000-2005) followed by a PhD (TU Dresden/TU Dortmund) on the mechanistic studies of the (un)catalyzed Gosteli-Claisen rearrangement (mentor Prof. Hiersemann). The Postdoctoral period was dedicated to investigating reaction-dynamic effects (non-statistical dynamics and reaction path bifurcations) in rearrangement reactions under the mentorship of Prof. Barry K. Carpenter. The independent career, first supported by the FCI and then by DFG (Emmy-Noether stipend), was started in 2012 in Hamburg. Since 2017, she holds a W2 professorship (Organic Chemistry) at the University of Regensburg and is interested in mechanism-driven method development, reaction-dynamics and properties of short-lived intermediates.