MANGANESE, CARBENES AND LIGHT – A SUCCESSFUL TRIPLE

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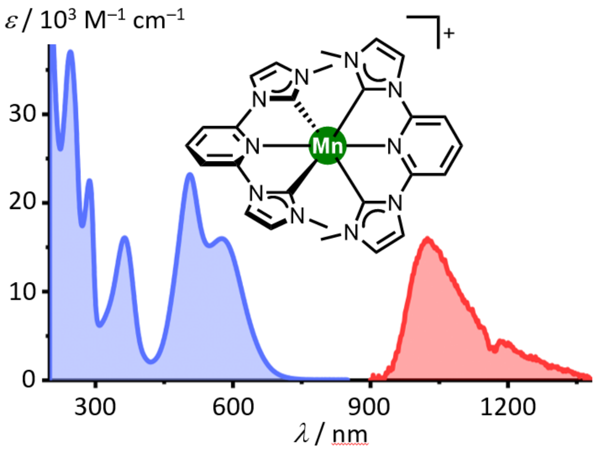
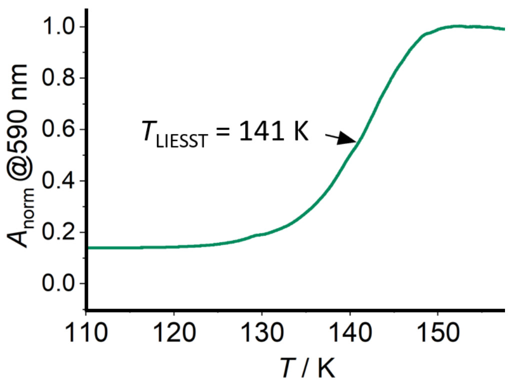
Compared to iron(II/III) complexes, the photophysics and photochemistry of isoelectronic carbene manganese(I/II) complexes is heavily underexplored. Our rationale to exploit the much higher covalency of Mn–C and Mn–N bonds as compared to the more ionic Fe–C and Fe–N bonds resulted in very high-energy ligand field states of the carbene manganese complexes. This led to the development of unusual low-spin manganese complexes with unique photophysical properties which were assessed by variable-temperature time-resolved emission and absorption spectroscopy:



The photophysics and photochemistry of the first low-spin carbene $3d^6$ manganese(I) complex $[Mn(pbmi)_2]^+$ resemble that of the classical precious-metal $4d^6$ complex $[Ru(bpy)_3]^{2+}$. The NIR-luminescent triplet metal-to-ligand-charge transfer (^{3}MLCT) state possesses an extremely long lifetime of 190 ns and is even capable of reducing benzophenone to its radical anion.[1]



One-electron oxidation delivers the corresponding low-spin $3d^5$ carbene manganese(II) complex $[Mn(pbmi)_2]^{2+}$: This complex remains in its low-spin state at all available temperatures but switches to the high-spin $3d^5$ state upon green light irradiation. $[Mn(pbmi)_2]^{2+}$ is the first manganese complex that shows this LIESST effect (light-induced excited spin state trapping) due to the large increase of Mn–C/N bond lengths of 0.282 and 0.377 Å during the low-spin-to-high-spin switching process as obtained by photo X-ray crystallography. The photomagnetic effect can be readily observed up to high temperature (T_{LIESST} = 141 K) allowing writing of magnetic information with light at convenient temperatures.[2]

[1] S. Kronenberger, R. Naumann, C. Förster, N. R. East, J. Klett, K. Heinze, *Nat. Commun.* **2025**, *16*, 7850.

[2] S. Kronenberger, R. Naumann, C. Förster, J. Klett, D. Schollmeyer, L. M. Carrella, E. Rentschler, K. Heinze, *Nat. Chem.* **2026**, accepted. Preprint: 10.26434/chemrxiv-2025-lrnqm.