

Long-lived triplet states in isomeric Zn(II) complexes with charge transfer character used in energy-transfer photocatalysis, electron transfer and upconversion

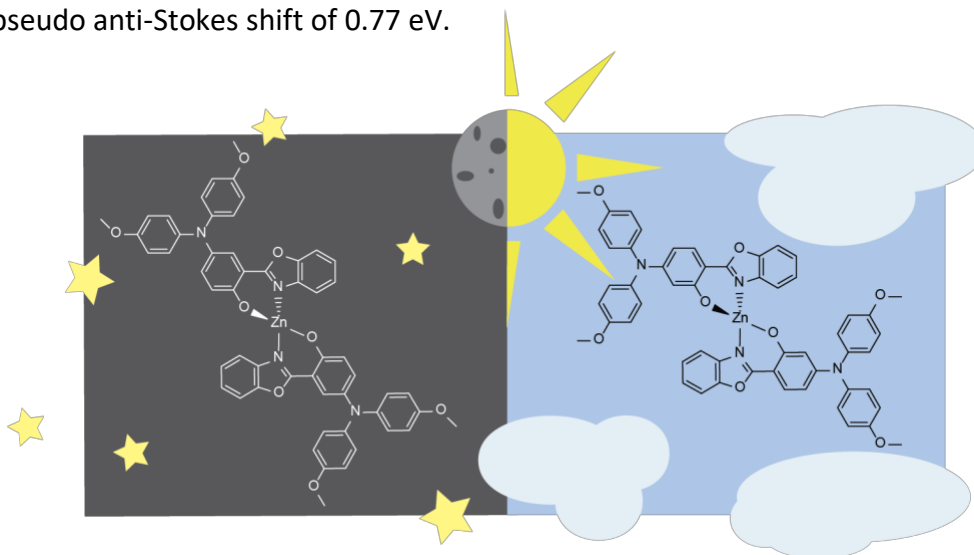
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Developing photoactive complexes based on first-row transition metals represents an important challenge in modern photochemistry. The completely filled valence orbitals in $3d^{10}$ metals renders metal-centred nonradiative deactivation pathways inefficient and can therefore lead to long-lived metal-to-ligand charge transfer (MLCT) excited states, as often observed in Cu(I) complexes.^[1,2] Zn(II) complexes in contrast have a higher oxidation state and the MLCT states are therefore shifted to higher energies.^[3] Thus, their photophysical and -chemical properties more typically rely on ligand-based excited states.

Two structural isomers of homoleptic, tetrahedral zinc(II) complexes with photoactive intraligand charge-transfer (ILCT) excited states are presented. Despite their structural similarity, they differ in photophysical properties: $[Zn(m-L)_2]$, the “night complex”, absorbs in the visible range and has more efficient intersystem crossing to its dark triplet state. The second complex, $[Zn(p-L)_2]$ or the “day complex”, in contrast has a higher fluorescence quantum yield and absorbs mainly in the UV region. DFT calculations suggest that $[Zn(m-L)_2]$ exhibits stronger charge-transfer character, which causes the observable differences in absorption and furthermore leads to different triplet energies and intersystem crossing efficiencies. Both complexes can be used in triplet-triplet energy transfer (TTET) photocatalysis, and laser flash photolysis experiments provided direct evidence for photoinduced electron transfer reactivity. Furthermore, the absorption properties of $[Zn(m-L)_2]$ qualify it as a sensitizer for the triplet-triplet annihilation upconversion from blue to UV with 1,4-bis((SiMe₃)ethynyl)naphthalene as annihilator, resulting in a pseudo anti-Stokes shift of 0.77 eV.



- [1] M. Ruthkosky, C. A. Kelly, F. N. Castellano, G. J. Meyer, *Coord. Chem. Rev.* **1998**, *171*, 309–322.
- [2] S. Garakyaraghi, C. E. McCusker, S. Khan, P. Koutnik, A. T. Bui, F. N. Castellano, *Inorg. Chem.* **2018**, *57*, 2296–2307.
- [3] O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533.