Combination of strong π- and σ-donating ligand yields a cobalt(III) complex with a long-lived MLCT excited state

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Rare and expensive $4d^6$ and $5d^6$ transition metal complexes with long-lived metal-to-ligand charge transfer (MLCT) excited states are widely used in various important applications of photophysics and photochemistry such as solar energy conversion, photodynamic therapy, photo(redox)catalysis and light emitting diodes. In this regard, cyclometalated Ir^{III} complexes with long-lived MLCT excited states are important class of compounds,[1] and often strong σ-donors and strong π-acceptors ligands are used to obtain such compounds. We are interested to obtain an isoelectronic Co^{III} complex with a MLCT excited state as both Ir and Co belong to the same group in the periodic table of elements. Our work aligns with the currently growing interest in photoactive first-row transition metal complexes.[2] When strong σ-donating ligands are used to obtain Co^{III} complexes, mainly ligand-to-metal charge transfer (LMCT) or metal-center (MC) excited states are usually obtained.[3,4] To achieve an elusive Co^{III} complex with substantial MLCT excited state character, we use an alternative ligand design strategy where a tridentate ligand is used, in which a strong π-donating amido donor and two strong σ-donating (weakly π-accepting) N-heterocyclic carbene (NHC) donors are combined (Figure 1). The newly developed Co^{III} complex has been characterized by NMR spectroscopy, mass spectrometry and X-ray crystallography, and its photophysical properties have been studied by cyclic voltammetry, UV-Vis spectroscopy, spectro-electrochemistry, ps-and fs-transient absorption spectroscopy in addition to DFT calculations. The present complex has a 1.2 ns MLCT excited state lifetime and can transfer an electron to methyl viologen dication upon blue light excitation.

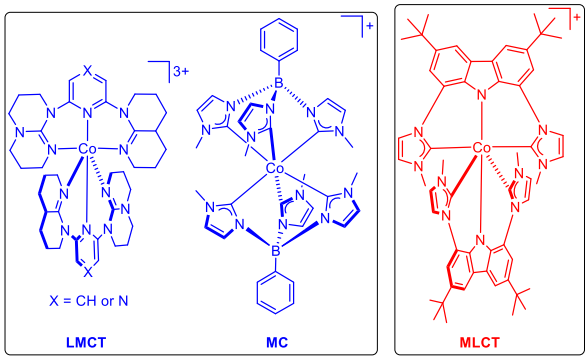

Figure 1. Previously studied (in blue) and present (in red) cobalt (III) complexes with different types of photoactive excited states.

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[3] A. K. Pal, C. Li, G. S. Hanan, E. Zysman-Colman, *Angew. Chem. Int. Ed.* **2018**, *57*, 8027–8031.
[4] S. Kaufhold, N. W. Rosemann, P. Chábera, L. Lindh, I. Bolano Losada, J. Uhlig, T. Pascher, D. Strand, K. Wärnmark, A. Yartsev, P. Persson, *J. Am. Chem. Soc.* **2021**, *143*, 1307–1312.