

MS36-P3 Red-light activated photoCORMs of Mn(I) species bearing symmetric substituted 2,2'-azopyridines.

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Carbon monoxide (CO) has been acknowledged as a fundamental neurotransmitter in humans and there is a growing interest in its pharmacological or medical applications. As nitric oxide and hydrogen sulfide, CO is endogenously produced in animals. These neurotransmitters are involved in several cellular, physiological and pathological pathways, such as vasodilatation, endothelial injuries, inflammation. Organometallic carbonyl complexes are best suited to play the role of CO carriers. Targeting of the molecules to local injuries can thus be achieved by modifying the coordination sphere of the metal ion via a proper selection of ligands or by appending CO releasing molecules (CORMs) to biomolecules. Manganese-based CORMs, for example, are activated by exposure to UV-light and are known as photoCORMs^[1]. One of the great challenges in the design of photoCORMs lies in their sensitivity to visible light. Most of known photoCORMs have suffered from this fundamental drawback with few exceptions. In particular the group of Mascharak^[2] has endeavored to develop rational strategies to visible light-activated CORMs and has introduced a series of carbonyl Mn(I) complexes with conjugated ligands of the 2-pyridyl-N-(2-methylthiophenyl) methylenimine and 2-phenylazopyridine type which show MLCT bands with maxima at ca. 585 nm. These molecules represent probably the most significant improvement the field has seen in the recent years. In this work, we report the synthesis, characterization and photochemical behaviour of the above mentioned complexes. The systematic substitution of the 2,2'-azopyridine with weak donating to strong deactivating substituents (EWG) lead to the progressive bathochromic shift of the MLCT absorption band maximum from 625 nm to 693 nm (Fig. 1). Exposure of solutions of complexes 1-5 to low-power visible light (≥ 625 nm, red light) resulted in CO photorelease as evidenced by the myoglobin assay. Furthermore, the MLCT band of complexes with strong EWG tails beyond the visible region of the spectrum in the near infrared and in one case photodecomposition could also be promoted at 810 nm. References: [1] Kottelat, E.; Chabert, V.; Crochet, A.; Fromm, K. M., Zobi, F., *Eur. J. Inorg. Chem.* **2015**, 34, 5628-5638 [2] Chakraborty, I.; Carrington S. J.; Mascharak, P., *Acc. Chem. Res.* **2014**, 47, 2603-2611

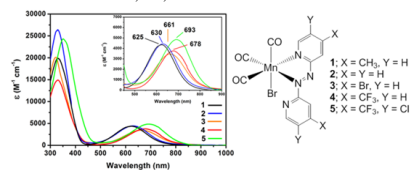


Figure 1. Electronic absorption spectra (left) and the molecular structure of $[\text{MnBr}(\text{azpy})(\text{CO})_2]$ species presented in this work (right).

Keywords: CO Releasing Molecules, Manganese, azopyridine