MANGANESE(II) COMPLEX WITH BIDENTATE NHC LIGAND AS CATALYST FOR CRP2

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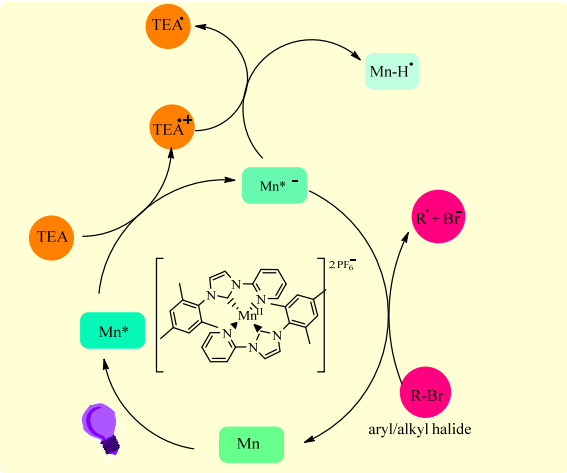

Figure 1. Reductive pathway for the CRP2 of MA catalyzed by the Mn^{II} complex in the presence of

The photoredox polymerization has been used as a green method to obtain well-defined polymers. One of the most studied methods is the *Controlled Radicalar Photopolimerization (CRP2)*.[1,2] The $[Mn^{II}(py\text{-mesethylimidazole})_2](PF_6)_2$ complex was synthesized from the NHC, *py*-mesethylimidazole, and further characterized. The *py*-mesethylimidazole ligand was characterized by FTIR, UV-Vis, fluorescence spectroscopy and 1H NMR. The complex $[Mn^{II}(py\text{-mesethylimidazole})_2](PF_6)_2$ was characterized by FTIR and UV-Vis, cyclic voltammetry, MALDi-TOF and fluorescence spectroscopy. The synthesized complex was additionally studied photophysically in the presence of polymerization additives at 365 nm, and where the Stern-Volmer constant (K_{SV} = 0.387 $moL^{-1}{\cdot}L$ was estimated. The behavior of the complex obtained was also monitored against irradiation at 365 nm, and its sensitivity to air. The synthesized complex was active as a photocatalyst in methyl acrylate (MA) CRP2, using α-ethyl-bromophenylacetate as initiator and triethylamine (TEA) as electron donor. The obtained polymers exhibited uniform masses with Đ < 2. The best condition for the photocatalysis was in the molar ratio of $[MA/EBr/Mn^{II}/TEA]$ = 200/1/0.12/1 with Mn = 160000 $g{\cdot}mol^{-1}$ and Đ = 1.4 with 73% conversion. The same ratio was used in the kinetic monitoring of the polymerization of methyl acrylate, showing that the complex, in addition to catalyzing a pseudo-first order reaction (k_{obs}= $2.1{\times}10^{-3}$ min^{-1}), keeps the system slightly controlled.

[1] Federico Bella, Roberta Bongiovanni. Photoinduced polymerization: An innovative, powerful and environmentally friendly technique for the preparation of polymer electrolytes for dye-sensitized solar cells. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 16, 1-21(2013).

[2] Mao Chen, Mingjiang Zhong, and Jeremiah A. Johnson. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. Chem. Rev. 116, 17, 10167–10211 (2016).