Photophysical properties of Re(I) complexes containing imidazole ligands: towards the application on CO_2 reduction

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Tricarbonyl rhenium complexes have been widely investigated as molecular photocatalysts for CO_2 reduction due to their chemical versatility and adjustable photophysical and photochemical properties [1]. In this work, we have synthesized two Re(I) complexes with imidazole ligands, *fac-Re*$(CO)_3$(pbiH)Cl and *fac*-Re$(CO)_3$(bbpz)Cl, where NN = 2-(2-pyridyl)benzimidazole (pbiH) and 2,6-bis(2-benzimidazolyl)pyridine (bbpz) aiming at the investigation of their photophysical properties and application as molecular catalysts for CO_2 reduction. The products were initially characterized by FTIR and ^{1}H NMR to confirm the molecular structure. The ^{1}H NMR are mainly characterized by peaks between 7 and 9 ppm, attributed to the hydrogen of the aromatic rings of the bbpz and pbiH ligands, which are shifted to lower field in relation to the signals of the non-coordinated species. Additionally, the acidic character of the imidazole proton from amine bonds present in the ligand is evidenced by a small and broad singlet between 13 and 15 ppm, due to equilibrium with the solvent used. FTIR data confirm the presence of ν_{N-H} m(≈3055), $\nu_{C\equiv O}$ s(≈2020, 1890 and 1870) and ν_{Re-N} m(≈260) stretches indicating the presence of the acidic imidazole proton, the *facial* geometry of the complex, and metal coordination mode. The photophysical properties of the complexes were investigated in acetonitrile solutions, Table 1. There is a red shift in the absorbance and emission maxima, along with a decrease in quantum emission yield (ϕ_{em}) and triplet oxygen yield (ϕ_{Δ}) when pbiH is replaced by bbpz. This behavior suggests the faster non-radiative deactivation of the Re$(CO)_3$(bbpz)Cl lowest-lying excited state. The hypsochromic shifts of the emission maxima observed for both complexes at glassy medium (77 K) indicate that both species are ^{3}MLCT emitters, but for *fac*-Re$(CO)_3$(pbiH)Cl, there is some evidence of a second contribution, likely ^{3}ILCT in nature. Finally, the complexes were tested as CO_2 photocatalysts, showing turnover numbers (TON) of 0.5 and 43 for Re$(CO)_3$(pbiH)Cl and Re$(CO)_3$(bbpz)Cl, respectively, after 3 hours. Mechanistic studies are in progress to rationalize the photocatalytic performance with the nature and relative energy of the respective excited states.

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References

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