

Advanced NHC-Based First-Row Metal Photocatalysts for Photopolymerization and 3D Printing

Naralyne M. Pesqueira^{*1,2}, Camila Bignardi^{1,2}, Valdemiro P. Carvalho Júnior¹, Jacques Lalevée^{2,3}, and Beatriz E. Goi¹

¹São Paulo State University (Unesp), School of Technology and Sciences, Presidente Prudente, SP, 19060-900, Brazil.

²Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France.

³Université de Strasbourg, F-67000 Strasbourg, France.

naralyne.pesqueira@unesp.br

Abstract

First-row transition metal complexes have gained attention as alternatives to noble metals in various reactions, particularly as efficient redox-active photocatalysts in photopolymerization reactions. In this study, Fe^{II}, Mn^{II}, and Ni^{II} complexes bearing *N*-heterocyclic carbene (NHC) ligands were evaluated as photocatalysts in free-radical photopolymerization (FRP). A three-component system composed of the photocatalyst (PC), di-tert-butyl-diphenyliodonium hexafluorophosphate (Iod), and ethyl dimethylaminobenzoate (EDB) was employed for FRP of ethoxylated trimethylolpropane triacrylate (TMPETA) under violet LED irradiation. The NHC-metal complexes exhibited promising photocatalytic performance under LED@405 nm. Moreover, the emissive nature of these complexes allowed for a comparative analysis of the influence of both the NHC ligand and the metal center, establishing a relationship between their optical properties and catalytic activity. The optimal condition was successfully applied in 3D printing, yielding well-defined 3D patterns.

Keywords: iron, manganese, nickel, NHC, photopolymerization, 3D printing.

Introduction

The use of first-row transition metal complexes bearing *N*-heterocyclic carbene (NHC) ligands has gained attention in organometallic chemistry due to their versatility in a wide range of applications, such as catalysis, CO₂ reduction, hydrogenation, dehydrogenation, and photopolymerization reactions(1,2). This interest arises from the need for efficient photocatalysts based on abundant and inexpensive metals operating under mild conditions. NHC ligands have shown promise in enhancing the luminescence of metal complexes by improving orbital overlap and providing strong σ -donation, thereby minimizing non-radiative decay(2).

To evaluate the photocatalytic performance of first-row transition metal–NHC complexes, Fe(II), Mn(II), and Ni(II) complexes with a pyridine-functionalized NHC ligand were synthesized to evaluate their photocatalytic performance in free-radical photopolymerization (FRP) under LED@405 nm (Figure 1). The three-component system with photocatalysts, Iod, EDB, and TMPETA monomer, was applied. In addition, these complexes were also tested in 3D printing applications.

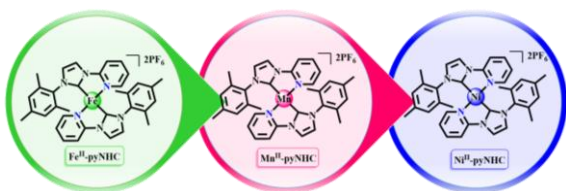


Figure 1. All the photocatalysts used in photopolymerization reactions.

Experimental

Synthesis of NHC-metal complexes

Mn^{II} and Ni^{II}–NHC complexes were synthesized as described in the literature(2,3). Fe^{II}–pyNHC was synthesized according to a modified literature procedure(2). A flask was charged with 0.243 g of NHC (py-Imes) and 0.100 g of KO^tBu. Three argon purge cycles were performed before the addition of 5 mL of previously degassed THF. After 5 hours, FeCl₂ (0.037 g) was added to a flask under argon atmosphere, and the NHC solution was transferred. The mixture was stirred overnight at room temperature. All volatiles were removed in vacuo, and the residue was extracted with 30 mL of CH₂Cl₂ and filtered. The solvent was removed in vacuo, and the residue was treated with ethyl ether, leading to the precipitation of a solid. The solid was collected by filtration, washed with ethyl ether, and dried in vacuo to yield a brown powder. (Figure 2).

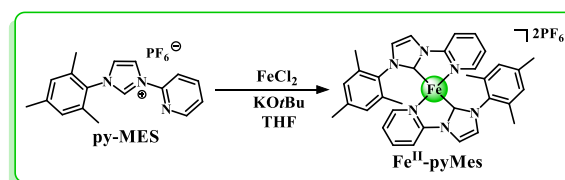


Figure 2. Synthesis of the Fe^{II}–pyNHC.

Yield: 45%, (0.235 g). a) FTIR (cm⁻¹): ν (C–H) 3157–2989, ν (C=N) 1608, ν (C=C) 1616, ν (PF₆) 842 and 558, ν (Fe–N) 450. b) UV-Vis λ_{max} (n) (nm), ϵ_{max} (n) (M⁻¹cm⁻¹): λ_{max} (1) 270, ϵ (1) 2390; λ_{max} (2) 320, ϵ (1) 1908; λ_{max} (3) 350, ϵ (3) 506.

Photopolymerization procedure

FRP was carried out using M^{II} /Iod/EDB systems (three-component systems) for **Fe^{II}-pyNHC**, **Mn^{II}-pyNHC** and **Ni^{II}-pyNHC**. The formulations were prepared in the mass ratio of TMPETA monomer: 0.1%/1%/1%, and 0.2%/2%/2% w/w/w for M^{II} /Iod/EDB. FRP. Thus, the formulation was deposited between two laminate (75 μ m thick). The systems were irradiated with LED@405 nm. In addition, the formulation was applied in 3D printing using a laser diode@405 nm(2,3).

Results and Discussion

Optical properties

The absorption properties of the organometallic complexes were investigated in CH_2Cl_2 at 25 °C. The NHC–metal complexes exhibited absorption at 405 nm, for which LED@405 nm was selected as the irradiation source for photopolymerization. **Mn^{II}-pyNHC** (345 mol L⁻¹cm⁻¹) showed higher molar absorptivity compared to **Fe^{II}-pyNHC** (ϵ_{405} = 190 mol L⁻¹cm⁻¹) and **Ni^{II}-pyNHC** (ϵ_{405} = 211 mol L⁻¹cm⁻¹). Both **Mn^{II}-pyNHC** and **Ni^{II}-pyNHC** emitted fluorescence in the blue region of the spectrum, while **Fe^{II}-pyNHC** showed emission from the blue to green range of the spectra. The lifetimes, measured in CH_2Cl_2 at 25 °C, were of 0.28, 3.3 and 3.8 for **Fe^{II}-pyNHC**, **Mn^{II}-pyNHC** and **Ni^{II}-pyNHC**, respectively.

Free radical photopolymerization

Free radical photopolymerization was evaluated using NHC–metal complexes (Fe, Mn, or Ni) in the presence of the TMPETA monomer, with iodonium salt (Iod) and ethyl 4-(dimethylamino)benzoate (EDB) as additives. The reactions were carried out under a laminate procedure using LED@405 nm, and the consumption of acrylate C=C bonds was monitored by FTIR at approximately 4700 and 6200 cm⁻¹(2,3). Under the condition 0.1%/1%/1% w/w/w (PC/Iod/EDB), **Ni^{II}-pyNHC** exhibited higher monomer conversion than the other complexes, reaching 91% within 300 s. However, **Mn^{II}-pyNHC** and **Fe^{II}-pyNHC** showed shorter inhibition times (Figure 3).

To investigate the effect of increased photocatalyst and additive amounts, the condition 0.2%/2%/2% (w/w/w) was also examined (Figure 4). Under these conditions, **Ni^{II}-pyNHC** demonstrated superior performance, achieving 98% conversion in a short period, while **Mn^{II}-pyNHC** and **Fe^{II}-pyNHC** exhibited lower conversions of approximately 40% and 60%, respectively. These results can be attributed to the photochemical properties of the complexes, as **Ni^{II}-pyNHC** exhibited a longer excited-state lifetime under the same experimental conditions. Furthermore, 3D patterns were obtained under optimal condition (0.2%/2%/2% w/w/w of PC/Iod/EDB) using NHC–metal complexes, exhibiting regular and smooth structures(2,3).

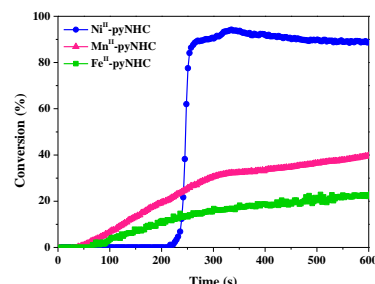


Figure 3. Conversion of TMPETA vs irradiation time under LED@405 nm in laminate, using 0.1%/1%/1% w/w/w M^{II} /Iod/EDB.

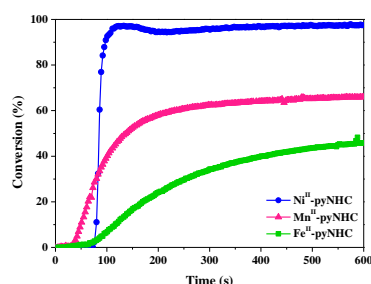


Figure 4. Conversion of TMPETA vs irradiation time under LED@405 nm in laminate, using 0.2%/2%/2% w/w/w M^{II} /Iod/EDB.

Conclusions

Fe^{II}-pyNHC was synthesized and characterized by spectroscopic techniques and MALDI-TOF mass spectrometry. Among the NHC-metal complexes evaluated, **Ni^{II}-pyNHC** exhibited the highest photocatalytic performance in FRP reactions. This behavior was attributed to the superior photochemical properties, including its longer excited-state lifetime.

Acknowledgments:

NMP, CB, VPCJ, and BEG are indebted to the financial support from FAPESP, grant #2021/11741-8, grant #2022/16571-6 and #2024/03026-5, grant #2021/13128-1, and grant #2025/04536-0, respectively, São Paulo Research Foundation (FAPESP).

References

- 1 M. L. B. Figueiredo, C. Bignardi, N. M. Pesqueira, A. E. H. Machado, V. P. Carvalho-Jr, O. R. Nascimento, and B. E. Goi, *J. Photochem. Photobiol. A Chem.*, **2024**, 452, 115567.
- 2 N. M. Pesqueira, F. Morlet-Savary, M. Schmitt, V. P. Carvalho-Jr, B. E. Goi and J. Lalevée, *Polym. Chem.*, **2025**, 16, 2436-2448.
- 3 C. Bignardi, N. M. Pesqueira, Y. M. Shimizo, A. E. H. Machado, D. M. S. Araújo, O. R. Nascimento, V. P. Carvalho-Jr, J. Lalevée, and B. E. Goi, *ACS Appl. Polym. Mater.*, **2025**, 7, 7429–7439.