New Mn(II) NHC complex photocatalyst for the CRP2 reactions

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Resumo/Abstract (Helvética, tam. 12)

RESUMO - O complexo [MnII(*py*-mes)2](PF6)2 foi sintetizado a partir do NHC, py-mesetilimidazol, e posteriormente caracterizado. O ligante py-mesetil foi caracterizado por FTIR, UV-Vis, espectroscopia de fluorescência e RMN de 1H e o complexo [MnII(*py*-mes)2](PF6)2 por FTIR e UV-Vis, voltametria cíclica, MALDi-TOF e espectroscopia de fluorescência. O complexo foi estudado fotofisicamente na presença dos aditivos da polimerização em 365 nm, tendo sido calculada a constante de Stern-Volmer (KSV = 0,387 M-1). Além disso, o comportamento do complexo obtido frente à irradiação em 365 nm também foi avaliado. O complexo sintetizado mostrou-se ativo como fotocatalisador na CRP2 do acrilato de metila (MA), utilizando α-bromofenilacetato (EBPA), como iniciador, e a trietilamina (TEA). Os polímeros obtidos apresentaram massas uniformes com Đ < 2. A melhor condição para a fotocatálise foi na razão molar de [MA/EBr/Mn/TEA] = 200/1/0,12/1 com Mn = 160000 g•mol‒1 e Đ = 1,4 com 73% de conversão. A mesma razão foi utilizada no acompanhamento cinético da polimerização, mostrando que o complexo além de catalisar uma reação de pseudo-primeira ordem (kobs= 2,1×10‒3 min‒1) mantém o sistema moderadamente controlado.

ABSTRACT – The [MnII(*py*-mes)2](PF6)2 complex was synthesized from the NHC, py-mesethylimidazole, and further characterized. The py-mesetil ligand was characterized by FTIR, UV-Vis, fluorescence spectroscopy and 1H NMR and the [MnII(*py*-mes)2](PF6)2 complex by FTIR and UV-Vis, cyclic voltammetry, MALDi-TOF and fluorescence spectroscopy. The complex was photophysically studied in the presence of polymerization additives at 365 nm, and the Stern-Volmer constant (KSV = 0.387 M-1) was calculated. Furthermore, the behavior of the complex obtained against irradiation at 365 nm was also evaluated. The synthesized complex was active as a photocatalyst in methyl acrylate (MA) CRP2, using α-bromophenylacetate (EBPA) as initiator and triethylamine (TEA). The obtained polymers presented uniform masses with Đ < 2. The best condition for the photocatalysis was in the molar ratio of [MA/EBr/Mn/TEA] = 200/1/0.12/1 with Mn = 160000 g•mol‒1 and Đ = 1.4 with 73% conversion. The same ratio was used in the polymerization kinetic follow-up, showing that the complex, in addition to catalyzing a pseudo-first order reaction (kobs= 2.1×10‒3 min‒1), keeps the system moderately controlled.

*Keywords* *N-heterocyclic carbenes, manganese(II), photacatalyst, CPR2*

## Introduction

These last decades, controlled/living radical polymerization (CRP) has been the subject of intense efforts and great attention.[1,2] More recently, the use of light in CRP has been introduced.[3]The controlled radical photopolymerization (CRP2) benefits of different advantages compared with CRP, including a spatial and temporal control of the polymerization reaction but also the possibility to carry out the polymer synthesis at room temperature to avoid undesired side reactions. CRP2 must be defined as a process where the light controls the opening of the dormant species (i.e., without light, the re-initiation does not take place). This is not a process where the initiation only is governed by light as with classical Type I or Type II photoinitiators (PI). CRP2 can offer many advantages: (i) the control of the molecular weight upon light irradiation, (ii) the copolymer synthesis at room temperature, (iii) the on/off polymerization on demand upon light irradiation, and (iv) surface modification and/or surface patterning that can be carried out with spatial control in the light irradiated area. The CRP2 reactions are based in the three-component initiating system.

The CRP2 can occur using organic or metal centered photocatalyst. Several families of PCs have been checked for the generation of radicals usable in polymerization reactions under very soft conditions[5–8] and their ability to operate in CRP2,[9] among them the Cu, Ru, Ir and Fe complexes. The reaction mechanisms are usually described by photoredox catalytic cycle (Fig. 1).



Figure 1. Mechanistic cycle for CRP2 reactions.

The first line transition metal complexes are considered promising to be used as photocatalysts. Numerous transition metal complexes such as V, Cr, Fe, Co, Ni, Cu, and Zn complexes have been explored as photocatalysts. With recent advances, manganese (Mn) has emerged as a valuable transition metal in reactions induced by visible light [10]. Catalysis using Mn promoted by visible light has recently evolved as a highly versatile tool to promote a wide range of organic transformations, being then able to induce organic reactions via photoinduced electron transfer. [11,12]A great attention should be focused on manganese complexes. Indeed, compared with very expensive and sometimes toxic Ir or Ru complexes, Manganese-based structures are quite cheap and potentially much less toxic opening up applications in the biomaterial area.

## Experimental

*Synthesis of Mn(II) complexes bearing NHCs ligands*

The synthesis of the Mn(II) complex was realized according to the following procedure: the NHC ligand (0.25 mmol), MnCl2 (0.125 mmol), KPF6 (0.25 mmol) and Cs2CO3 (0.375  mmol) was taken in a Schlenk flask and will be subjected to vacuum for 30 min. Acetonitrile (20 mL) was added, and then the reaction mixture was refluxed for 12 h to obtain a yellow colored suspension. All the volatiles were removed under vacuum, yielding a pale-yellow colored residue. The residue was washed with water to remove the leftover base and inorganic by products. The residue was washed with methanol (15 mL) and filtered through an open frit. The leftover residue was dissolved in CH2Cl2 and filtered. After, the solvent was evaporated under reduced pressure and the resulting powders were recrystallized in diethyl ether and pentane (1:2 ratio).

*General procedure for CRP2*

The photopolymerization procedure for monomer (MMA, MA, BA, or PEGDA) was prepareed as follows: a mixture solution was obtained by adding the MnII complexes, EDB (ethyl-4-(dimethylamino) benzoate), EBr (ethyl *a*-bromophenylacetate) and monomer to a dried Schlenk flask (25 mL) with a stir bar. The solution was deoxygenated through three standard freeze-pump-thaw cycles, flame-sealed, and placed in a stirring apparatus under LED irradiation. The samples was regularly collected from the medium using a nitrogen flushed syringe. The monomer conversion was evaluated by FTIR to determine conversion and SEC-THF to obtain molecular parameters using PMMA standards.

## Results and discussion

1. *Ligand and Mn Complex synthesis and characterizations.*

The imidazole was prepared by a classical route. For the synthesis of 1-Mesethylimidazole, the most suitable route is the one proposed by Gridnev (1994). In order to obtain mesethylimidazole, the reaction started with the mesethylaniline salt with glyoxal, in an acid medium, using paraformaldehyde and ammonium chloride to cyclize imidazole. To obtain the pure product, it wasextracted in hexane, precipitated and recrystallized in a mixture of CH2Cl2 and Et2O. In order to give the disubstituted imidazole (*py*-mesethylimidazole), the mesethylimidazole was reacted with the 2-bromepyridine. The respective Mn complex was synthetized from the deprotonation of the *py*-mesthylimidazole ligand in MeCN3 and the MnCl2 salt.

The imidazole precursor and the py-mesethylimidazol were both characterized by H1 NMR. It is noted that the 6 hydrogens referring to the methyls ortho positioned in the mesethyl substituent appear with a very intense signal at 1.96 ppm, while the 3 H referring to the methyl para positioned appear with a signal in 2.34 ppm, in both products. The second step for the synthesis of di-substituted NHC can be confirmed by 1H NMR in CDCl3. From the spectrum, it is possible to observe that the peak referring to hydrogen A appears at 11.50 ppm while in the imidazole monosubstituted spectrum, it is found around 6.95 ppm. The shift is observed due to the addition of bromopyridine to imidazole, which is a π-leaving group and makes hydrogen more acidic.

The ligand and the complex were characterized by FT-IR spectroscopy. From Figure 2, it is possible to observe that the bands referring to the Py-mesethyl(PF6) ligand remained in the complex, however the bands referring to the C‒H stretch were covered by an enlarged band that appears at 3500 cm‒1. Note a displacement in the stretch referring to the binding of azomethine, of 1608‒1604 cm‒1, indicating coordination of the N of pyridine with the metal center of MnII. The bands referring to the vibrations related to the free PF6‒ ion can still be observed around 842 and 558 cm‒1. In the region of 417 cm‒1, the appearance of a band referring to the stretching related to the Mn‒N bond is observed.



Figure 2. Vibrational absorption spectra in the infrared region for the compound [MnII(py-mesetyl)], and its starting reagents, MnCl2 and py-mesethylimidazole(PF6)2.

MALDi-TOF mass spectrometry analyzes of the [MnII(py-mesetil)2](PF6)2 complex were performed in CH2Cl2 and the detected metal ion data are shown in Figure 3. The spectrum of the complex shows the expected molecular ion [M2+] with sign at 291.8654 m/z, considering the m/2z ratio. The highest intensity peak found around 264.5678 m/z refers to free carbene. The more distant peaks are related to the alpha-cyano-4-hydroxycinnamic acid (HAAC) matrix.



Figure 3. MALDi-TOF spectrum for complex [MnII(*py*-mes)2](PF6)2.

The initial characterization of the py-mesithyl(PF6) ligand of the respective complex [MnII(py-mesithyl)2](PF6)2 by spectroscopy in the UV-Vis region (Figure 4) consisted of observing the difference between the absorption bands of the synthesized complex in comparison with the previously prepared NHC ligand. From the spectrum of the py-mesithyl (PF6) ligand, two bands related to the π‒π\* and n‒π\* electronic transitions at 245 and 266 nm, respectively. Comparing with the synthesized MnII complex, it is observed a hypsochromic shift of the band at π‒π\* from 245 to 240 nm, and for the band at 266 nm there is a bathochromic shift to 271 nm. In addition to these shifted bands, we observe the appearance of a shoulder at 312 nm related to n‒π\* transitions, and a band at 365 nm attributed to MLCT transitions.



Figure 4. UV-Vis spectra for the compounds py-mesithyl (PF6) and its respective complex [MnII(py-mesethyl)].

The [MnII(py-mesethyl)2](PF6)2 and the NHC were further characterized by photoluminescence spectroscopy. The complex has showed emission around 400 nm when excited with wavelength fixed at 320 nm as can be seen from figure 5. Also from this figure, it is possible to notice that when the complex was excited with wavelength fixed at 365 nm, the emission was discrete.

In order to study the luminescent behavior of the [MnII(*py*-mesetil)2](PF6)2 complex against solvents of different polarities, four fluorescence measurements were performed, as shown in figure 6.



Figure 5. Emission spectrum for the [MnII(py-mesithyl)2](PF6)2 complex in different solvents at 320 nm.

The solvatochromism investigation was carried out in four different solvents, acetonitrile, acetone, dichloromethane and methanol. It can be observed that the emission spectra in dichloromethane and acetone obtained the similar profile with a small shift between the absorption maxima, at 415 and 426 nm respectively. The spectrum in methanol presented its maximum absorption around 352 nm. Finally, the last solvent studied was acetonitrile, which has two emission bands, one at 360 and another at 430 nm. These differences in the spectra are linked to the polarity of the solvents, and also to the coordinating capacity of acetonitrile. In addition, we can also observe that dichlormethane, acetone and acetonitrile solvents are aporotic polar. The order of the dielectric constants arranged in ascending order is:

**dichloromethane < acetone < methanol < acetonitrile**

To better study the behavior of the complex against polymerization, fluorescence studies were carried out with additives added to the reaction (TEA). Figure 7 shows the behavior obtained in the spectrum of the complex [MnII(*py*-mesetil)2](PF6)2 after successive additions of TEA. From Figure 32, a suppression behavior is observed, with a decrease in emission intensity with the addition of TEA aliquots. The luminescence of a molecule can be suppressed by a series of photophysical/photochemical processes, or even by the presence of solvents/reagents that lead to deactivation by a radiative or non-radiative process.



Figure 6. Fluorescence spectrum for [MnII(*py*-mesethyl)2](PF6)2 complex in the presence of different TEA concentrations with excitation set at 365 nm.

From the intensity values obtained in Figure 7 and the TEA concentration used, it is possible to construct the Stern-Volmer plot ([suppressor] vs. I0/It), shown in Figure 8.



Figure 7. Stern-Volmer kinetic plot for the [MnII(*py*-mesetil)2](PF6)2 complex in the presence of TEA.

From the slope of the line obtained in Figure 8, it is possible to calculate the value of KSV. For the complex [MnII(*py*-mesitil)2](PF6)2 in the presence of TEA, Ksv = 0.387 M‒1 was obtained. The value obtained is lower than that found in the literature for transition complexes with other metallic centers. The Stern-Volmer constant also indicates the sensitivity of a fluorophore to a suppressor, if the fluorophore is free in solution, it will have lower KSV values.

To evaluate the catalytic activity of the [MnII(py-mesetil)] complex, some initial experiments were performed. The first test was performed without the presence of light, using Methyl Acrylate (MA) as monomer, α-bromophenylacetate (EBr) as initiator, Mn complex as photocatalyst and triethylamine (TEA) as electron donor, following the reductive route, using molar ratios [200/1/0.02/1], respectively, but there was no polymerization. The second test was carried out in the presence of light (365 nm LED) without the MnII complex, in which polymer formation was also not observed. Finally, photopolymerization of MA in CH2Cl2 using MnII/EBr/TEA was performed at 365 nm for 90 minutes at 25 ºC. At the end of the irradiation, an aliquot was taken to calculate the conversion and, subsequently, the sample was solubilized in THF, filtered and injected into SEC to obtain the values of Mn and Đ. The conversion found was around 35% while the Mn=144000g.mol‒1 and Đ=1.5. In order to investigate an ideal condition, some parameters were varied and are presented in Table 1.

Table 1. Conditions for photopolymerization catalyzed by the [MnII(*py*-mesitil)2](PF6)2 complex.

1. *Polymerization kinetics for the MA/EBPA/Mn/TEA system.*

The kinetic monitoring of the photopolymerization of the MA was carried out at the ratio of 200/1/0.12/01 in the [MA/EBPA/Mn/TEA] system with LEDs at 365 nm, which showed better results in the tests performed previously. Photopolymerization was followed for 330 minutes, where aliquots were taken every 30 minutes and analyzed by FTIR in order to calculate the conversion for each point. The data are summarized in table 2.

Table 2. Conversion values, molar mass and polydispersity obtained in the CRP2 of MA, in the ratio of 200/1/0.12/1 at 25ºC.

In Figure 8, the monomer conversion as a function of irradiation time can be seen, in which, based on the conversion values, it is possible to establish the order of the reaction. The inserted graph contains the dependency of ln([MA]0/[MA]t) as a function of reaction time as well.

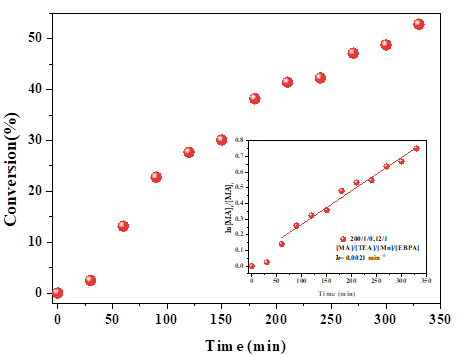


Figure 8. Dependence of time-varying conversion to CRP2 from methyl acrylate with [MnII(py-memethyl)2](PF6)2 complex at the molar ratio [MA]/[EBPA]/[MnII]/[TPO] of 200 /1/0.12/1 at 25°C for 360 minutes.

Performing the derivative of the conversion curve as a function of the reaction time (Figure 8), the dependence of the polymerization rate as a function of the monomer conversion is obtained, represented in Figure 9. According to the Figure 9, it can be observed that in the initial minutes there is a rapid increase in the polymerization speed, since the termination reactions are controlled by diffusion. This phenomenon is called self-acceleration (a). Then, the propagation reactions also become diffusion-controlled, leading to self-deceleration (b). However, the high viscosity in the polymeric medium makes it difficult to terminate the macroradicals by sequential movement (c). Consequently, the growth of the radical chain occurs through its propagation with the monomer that has not yet reacted until it encounters a second radical chain, thus, the termination occurs.

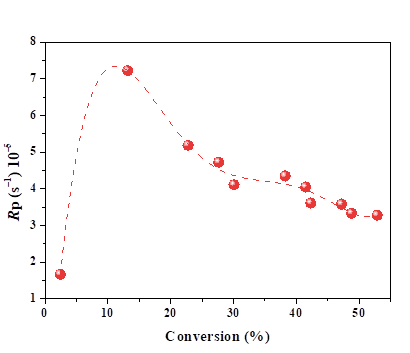


Figure 9. Dependency of polymerization rate (Rp) as a function of methyl acrylate conversion.

From Figure 10, one can observe an almost linear behavior between the increase in molar mass with the increase in conversion. During photopolymerization, a decrease in polydispersity index values is also observed, from 2.3 to 1.4, indicating a possible ability to control the system.



Figure 10. Dependency of MnGPC and Đ values with conversion to MA polymerization.

1. *UV-Vis polymerization kinetics and possible polymerization mechanisms*

In order to analyze the behavior of the complex [MnII(*py*-mesithyl)2](PF6)2 as a redox photocatalyst, an experiment based on the literature was proposed, in which a simulation of the polymerization is carried out, accompanied by UV-spectroscopy. Vis. For this, a solution was prepared containing the photocatalyst, the Methyl Acrylate (MA) monomer, and the initiator (EBr), as shown in Figure 12.



Figure 11. UV-Vis spectrum obtained from the simulation of polymerization in the photoreactor using the MnII complex as photocatalyst.

From figure 11 it is possible to observe the formation of an isosbetic point. This indicates the possible equilibrium between the species that are being formed and consumed. From the literature, it is possible to infer the formation of photoproducts after the addition of TEA in the system. The interaction of the MnII complex with TEA can form an exciplex in the excited state, according to the proposed mechanism for redox photocatalysts,11 as depicted is figure 12. The fact that the TEA act as a suppressor of the MnII\* also corroborates for the mechanism represented bellow.

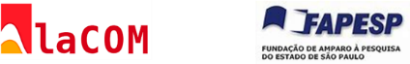
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Figure 12.Proposed mechanism for the interaction between TEA and the MnII complex when it is excited by a light source, via the reductive pathway.

Conclusions

The monosubstituted imidazole 1-H-mesethylimidazole was synthesized according to the literature and characterized by FTIR, UV-Vis and 1H NMR. Coupling reaction with 2-bromopyridine took place and the final ligand was characterized by FTIR, UV-Vis and 1H NMR satisfactorily. The Mn,II complex [MnII(py-mesithyl)2](PF6)2 was synthesized and initially characterized by FTIR, UV-Vis, cyclic voltammetry, fluorescence spectroscopy and DFT calculations. Photocatalysis studies showed that the complex [MnII(py-mesithyl)2](PF6)2 has a good catalytic activity, being able to polymerize MA in a three-component system in CRP2, using TEA as co-initiator, EBr as initiator, in bulk with molar masses around 105 g.mol‒1 with Đ ≥ 1.4. The [MnII(*py*-mesethyl)2](PF6)2 complex was studied photophysically in the presence of polymerization additives at 365 nm, where it was possible to calculate the Stern-Volmer constant (KSV = 0.387 M-1). The polymerization was simulated in UV-Vis using CH2Cl2 as solvent, the resulting spectra suggest the interaction of TEA with [MnII(*py*-mesithyl)2](PF6)2, as well as the formation and consumption of new species in the medium. The polymerization of MA with the MnII(*py*-mesithyl)2](PF6)2 complex was carried out at a molar ratio of 200/1/0.12/1 with kinetic monitoring of the polymerization of methyl acrylate, showing that the complex, in addition to catalyzing a pseudo-first order reaction (kobs= 2.1×10‒3 min‒1) keeps the system moderately controlled in a reaction followed for approximately six hours with 56% conversion, Mn = 170000 and IPD = 1.4.

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## Referências

1- Federico Bella, Roberta Bongiovanni.. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 16, 1-21.(2013)

2- Mao Chen, Mingjiang Zhong, and Jeremiah A. Johnson Chem. Rev. 116, 17, 10167–10211 (2016).

3- Andrzejewska E, Grajek K. MOJ Poly Sci. 2017;1(2):58-60.

4- Yusuf Yagci. Macromol. Symp. 161, 19–35 (2000).

5- Dietlin, C., Schweizer, S., Xiao, P., Zhang, J., Morlet-Savary, F., Graff, B., Lalevée, J. Polymer Chemistry, 6(21), 3895–3912. (2015).

6- N. Zivic, M. Bouzrati-Zerelli, A. Kermagoret, F. Dumur, J.-P. Fouassier, D. Gigmes, J. Lalevée,. ChemCatChem, 8, 1617.(2016)

7- Liang, E. X., Lu, M., Hou, Z. H., Huang, Y., He, B. H., Wang, G. X., Liu, L. C., Wu, H. and Zhong, M. (2015),. J. Appl. Polym. Sci., 133, 42891

8- Jean-Pierre Fouassier, Jacques Lalevée. Ed Wiley & Sons. Abril,2021. ISBN: 978-3-527-82126-6

9- Allushi, A., Kutahya, C., Aydogan, C., Kreutzer, J., Yilmaz, G., & Yagci, Y. Polymer Chemistry, 8(12), 1972–1977. (2017).

10- S. Telitel, F. Dumur, S. Telitel, O. Soppera, M. Lepeltier, Y. Guillaneuf, J. Poly, F. Morlet-Savary, P. Fioux, J.-P. Fouassier, D. Gigmes, J. Lalevée, Polym. Chem. 2015, 6, 613–624.

11- Jean Pierre Fouassier, Jacques Lalevee. Photoinitiators for Polymer Synthesis: Scope, Reactivity and Efficiency. Wiley & Sons. 2012, Alemanha.

12- Jean P. Fouassier, Jacques Lalevee. Photopolymerisation Initiating Systems. Ed. 29, Royal Society of Chemistry, Cambridge. (2018)

1. Endereço atual. [↑](#endnote-ref-1)