

Visible-Light-Activated Ni(II) Complexes as Photocatalysts for Radical Photopolymerization under LED Irradiation

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Abstract

Nickel(II) complexes have gained significant attention as efficient redox-active photocatalysts in photopolymerization processes. In this study, two Ni(II) complexes containing phenanthroline ligands were successfully synthesized and fully characterized using FTIR, UV-Vis and fluorescence spectroscopy, along with MALDI-TOF mass spectrometry. Their performance as photocatalysts was investigated in the free radical photopolymerization (FRP) of ethoxylated trimethylolpropane triacrylate (TMPETA) under violet and blue LED irradiation. A three-component photoinitiating system comprising a nickel complex, either di-tert-butyl-diphenyl iodonium hexafluorophosphate (Iod) or phenacyl bromide (Ph-Br), and ethyl dimethylaminobenzoate (EDB) was tested under LED irradiation. The nickel complexes demonstrated effective photoinitiation, leading to high monomer conversion rates and revealing clear structure–reactivity relationships. The Ni(II) complex with higher absorption and fluorescence properties exhibited superior catalytic performance under both Iod/EDB and Ph-Br/EDB conditions.

Keywords: nickel, fluorescence, free radical photopolymerization, TMPETA, LED irradiation.

Introduction

The photopolymerization reaction is one of the most efficient technologies for producing fast-curing products, such as films and coatings(1,2). It uses photons to initiate photochemical reactions in organic systems, converting them into polymeric materials and increasing molar mass during irradiation. Photopolymerization is widely applied in various industrial and laboratory area, with applications including radiation curing, laser imaging, 3D printing, microelectronics, optics, biosciences, dentistry, and nanotechnology. Moreover, radiation curing is recognized as an evolving green technology(1–3).

Photoinitiators convert light energy into chemical energy, generating reactive species (radicals or cations) that initiate the polymerization chain reaction(1). A significant improvement in three-component photoinitiating systems occurs when photoinitiators (PIs) are regenerated during the process, acting as photocatalysts (PCs)(1). In photoinitiating systems (PISs), photocatalysts enhance system efficiency by being regenerated in the catalytic cycle, requiring reduced amounts of photoinitiator and/or lower light intensity, thus improving the system's photosensitivity(1).

Photopolymerization involves both oxidative and reductive chemical pathways. Light excites redox-active photocatalysts, leading electron transfer with additives(1). The advantage of photoredox catalysis is its high efficiency under mild irradiation, as the catalyst is regenerated and only small quantities are needed. The catalytic cycle is maintained by regenerating the photocatalyst through the addition of either a reductant or an oxidant(1,2).

To enhance the photochemistry and performance of photoinitiating systems, Ni(II) complexes with different phenanthroline ligands are being explored. Initially, two Ni(II) complexes were synthesized following literature procedures. These complexes were subsequently characterized by spectroscopic techniques, including FTIR, UV-Vis, fluorescence, and MALDI-TOF spectrometry. Photopolymerization reactions were carried out using the Ni(II) complexes in the presence of phenacyl bromide (Ph-Br), diphenyl iodonium hexafluorophosphate (Iod), and ethyl dimethylaminobenzoate (EDB) as additives and ethoxylated trimethylolpropane triacrylate (TMPETA) as monomer (Figure 1). The catalytic activity of the Ni(II) complexes was evaluated in a three-component system: photocatalyst/Iod or Ph-Br/EDB under different LED irradiations (365, 390-405, and 420 nm).

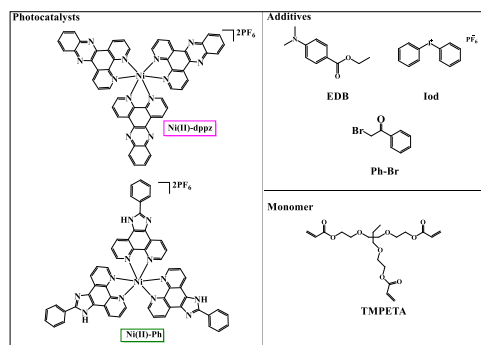


Figure 1. All the photocatalysts, additives and monomer used in photopolymerization reaction.

Experimental

Synthesis of functionalized ligands

The synthesis of the **Ph-ImPhen** ligand was carried out as described in the literature(4). The solution containing 1,10-phenanthroline-5,6-dione (5 mmol), benzaldehyde (6 mmol), ammonium acetate (100 mmol), and glacial acetic acid (16 mL) was heated under reflux with constant stirring for 3 hours. After cooling, the mixture was diluted with water and neutralized with concentrated ammonia in an aqueous medium. The resulting precipitate was collected. Yield: 80% (Figure 2).

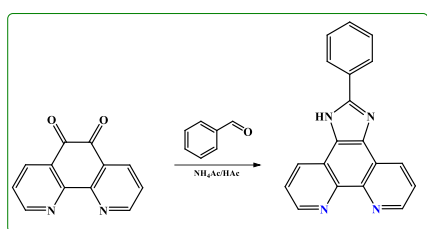


Figure 2. Synthesis of the **Ph-ImPhen** ligand.

The synthesis of the **dppz** ligand was performed as described in the literature(4). Initially, a solution of *o*-phenylenediamine (7.5 mmol) in ethanol was added dropwise to a solution of 1,10-phenanthroline-5,6-dione (5 mmol) previously dissolved in ethanol (20 mL). The resulting mixture was heated under reflux with constant stirring for 4 hours. After, the solution was concentrated under vacuum, and the formed solid was recrystallized from methanol. Yield: 75% (Figure 3).

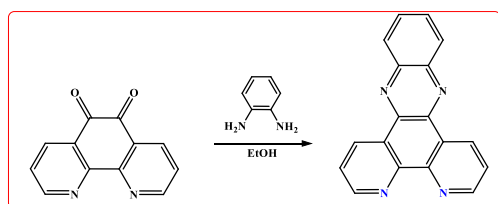


Figure 3. Synthesis of the **dppz** ligand.

Synthesis of Ni(II) complexes

The synthesis of the Ni(II) complexes was performed with modifications to procedures previously reported in the literature(4,5). Nickel(II) chloride hexahydrate (1 mmol) was added to 10 mL of a methanolic solution containing the corresponding ligand (3.3 mmol) and KPF₆ (2 mmol), followed by stirring for 15 minutes. The mixture was then heated under reflux during 24 hours. After cooling to room temperature, the resulting precipitate was collected by filtration and washed with cold methanol. The solid was recrystallized twice from DMF. Yield: ~70% (Figure 4).

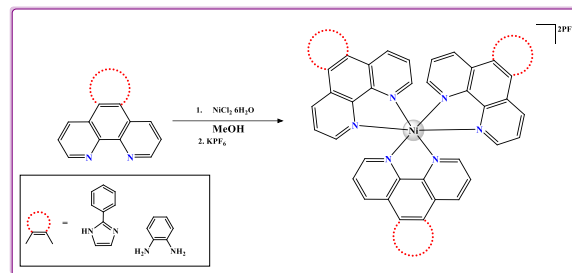


Figure 4. Synthesis of the Ni(II) complexes

Photopolymerization procedure

The free radical photopolymerization of TMPETA was carried out using Ni/Iod/EDB systems (three-component systems) for **Ni(II)-Ph** and **Ni(II)-dppz**. The formulations were prepared in the mass ratio of monomer: 0.2%/3%/3%, w/w/w for Ni/Iod/EDB or Ph-Br/EDB, respectively. Thus, the formulation was deposited in laminate (75 μm thick). The systems were irradiated with LED@365 nm, LED@390-405 nm or LED@420 nm.

Results and Discussion

The ligands were fully characterized by NMR, FTIR, and UV-Vis spectroscopy. The Ni(II) complexes were characterized by FTIR, UV-Vis, fluorescence spectroscopy, and MALDI-TOF mass spectrometry. NMR characterization was not feasible due to their paramagnetic nature.

¹H NMR of the ligands

The hydrogen signals of the ligands were identified based on the literature(4). For **Ph-ImPhen**, the two most acidic hydrogens were identified at 8.5 ppm, while the hydrogens at the *p*-position of the phenanthroline ring appeared at 8.3 ppm. The hydrogen at the *m*-position of the phenanthroline ring was observed at 7.8 ppm. The hydrogens of the phenyl group appeared between 7.0 and 7.5 ppm. For **dppz**, the most acidic hydrogens appeared as doublets at 9.7 and 9.4 ppm. Subsequently, the hydrogens at 8.4 and 7.9 ppm were assigned to the group derived from *o*-phenylenediamine, while the least acidic hydrogen appeared at 7.8 ppm.

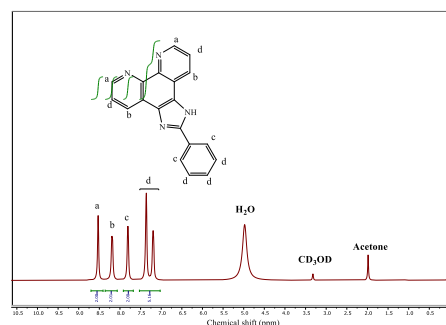


Figure 5. ¹H NMR spectrum of **Ph-ImPhen** in CD₃OD.

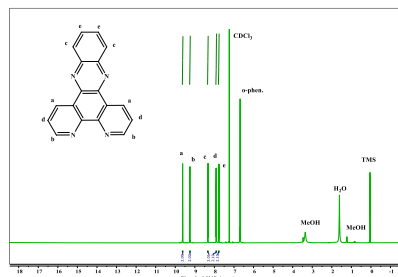


Figure 6. ^1H NMR of **dppz** in CDCl_3

FTIR of the ligands and Ni(II) complexes

The FTIR spectra of the Ni(II) complexes and ligands were compared and are shown in Figures 7 and 8. FTIR spectra of the precursor and the ligand displayed a leftward shift in the bands, indicating an increase in the wavenumber. The band corresponding to the C=N bond, at 1614 cm^{-1} , shifted to 1645 cm^{-1} , while the C=C band, initially at 1454 cm^{-1} , shifted to 1450 cm^{-1} . In the comparison between KPF_6 , **Ph-ImPhen**, and the **Ni(II)-Ph** complex, the PF_6^- band was retained but shifted to 845 cm^{-1} , and a new band at 425 cm^{-1} , attributed to Ni-N stretching, indicating metal coordination (Figure 7). For **Ni(II)-dppz** and **dppz**, the same stretching were found in similar regions, as observed in the Figure 8.

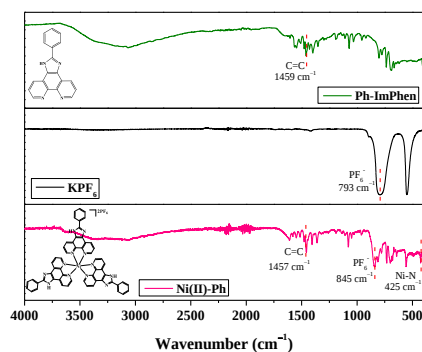


Figure 7. FTIR spectra of **Ni(II)-Ph** (pink line), KPF_6 (black line) and **Ph-ImPhen** (green line).

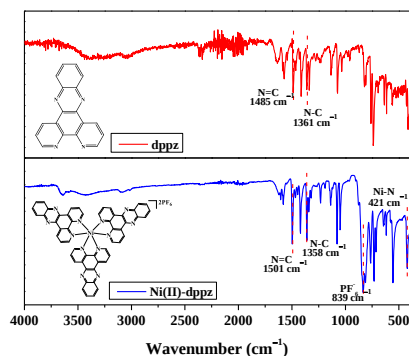


Figure 8. FTIR spectra of **Ni(II)-dppz** (blue line) and **dppz** (red line).

UV-Vis of the ligands and Ni(II) complexes

The absorption spectra of the Ni(II) complexes and ligands were evaluated at $1 \times 10^{-5}\text{ mol L}^{-1}$ in DMF (Figures 9 and 10). The bands associated with the $\pi \rightarrow \pi^*$ electronic transition are observed at 257 nm, 275 nm, and 320 nm for the ligands. When compared to the synthesized Ni(II) complex, a bathochromic shift is observed for the $\pi \rightarrow \pi^*$ transition, from 275 nm to 281 nm, and from 320 nm to 332 nm. In addition to these shifted bands, a new peak appears at 297 nm, related to $\pi \rightarrow \pi^*$ transitions, and a bathochromic shift is also observed for a band, from 372 nm to 392 nm, corresponding to $n \rightarrow \pi^*$ transitions. The bands above 390 nm can be attributed to the CT (charge transfer) transitions(4,5).

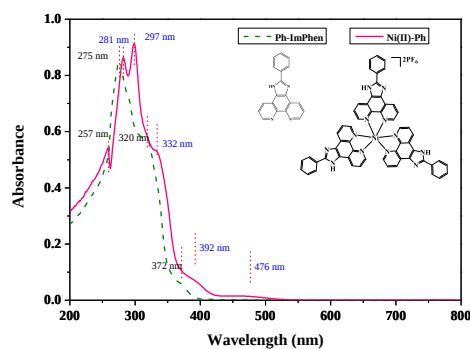


Figure 9. UV-Vis spectra of **Ni(II)-Ph** (pink solid line) and **Ph-ImPhen** (green dash line) in DMF at 25°C .

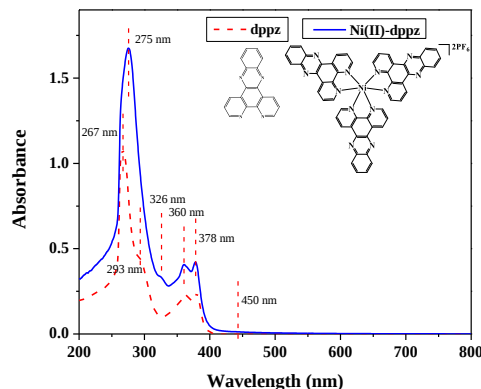


Figure 10. UV-Vis spectra of **Ni(II)-dppz** (blue solid line) and **dppz** (red dash line) in DMF at 25°C .

The molar absorptivity at 365, 390–405, and 420 nm was determined for the Ni(II) complexes. **Ni(II)-dppz** exhibited ϵ values of 39560, 13660–3170, and $1800\text{ M}^{-1}\text{cm}^{-1}$, while **Ni(II)-Ph** showed ϵ values of 12680, 7430–4800, and $1940\text{ M}^{-1}\text{cm}^{-1}$ (Figure 11). Thus, the LEDs were adequate for carrying out the photopolymerization experiments.

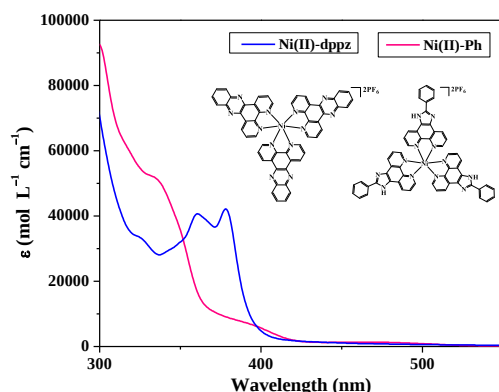


Figure 11. UV-Vis spectra of **Ni(II)-dppz** (blue line) and **Ni(II)-Ph** (pink line) in DMF at 25 °C.

MALDI-TOF of the Ni(II) complexes

The **Ni(II)-Ph** complex has not been reported in the literature, and therefore, an analysis was performed to confirm the structure of the intended complex. In this analysis, the sample is ionized with one or more protons (H^+), generating a molecular ion that subsequently undergoes a series of fragmentations. The mass spectrum represents the relative abundance of each ion (molecular ion and fragments) in relation to the mass-to-charge ratio (m/z). MALDI-TOF mass spectrometry of the complex was conducted in methanol. Upon examining the MALDI-TOF spectrum of **Ni(II)-Ph**, shown in Figure 12, a peak corresponding precisely to the mass of the complex at 648 m/z , along with the mass of the matrix, is observed, confirming the presence of the desired species. Additionally, an extra peak is observed, which may be attributed to the interaction between the complex and two matrix masses used in the analysis.

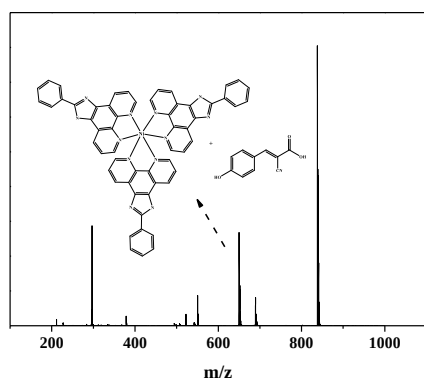


Figure 12. MALDI-TOF of **Ni(II)-Ph**.

Fluorescence of the Ni(II) complexes

The emission properties of the Ni(II) complexes were evaluated in methanol at 25 °C (Figure 13). **Ni(II)-dppz** exhibited more intense emission upon excitation at 360 nm compared to **Ni(II)-Ph**, which was excited at 330 nm.

Additionally, no emission was observed at higher wavelengths for either complex.

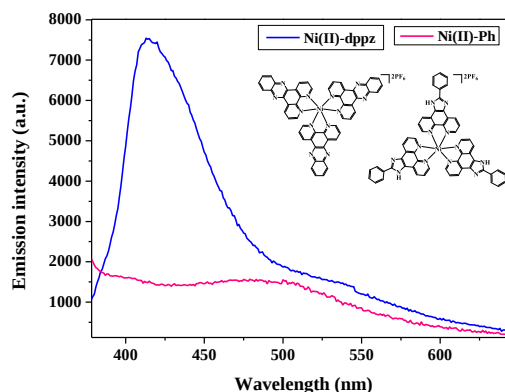


Figure 13. Emission spectra of **Ni(II)-dppz** (blue line) and **Ni(II)-Ph** (pink line). $[Ni] = 1 \times 10^{-5} \text{ mol L}^{-1}$.

Free radical photopolymerization

The free radical photopolymerization was investigated using Ni(II)-based photoinitiating systems (Ni/Iod/EDB or Ni/PhBr/EDB) in the presence of the TMPETA monomer (Table 1). The experiments were performed under different irradiation conditions with LED sources at 365 nm, 390–405 nm, and 420 nm. The formulations included 0.2 w% of the photocatalyst, 3 w% of the iodonium salt, and 3 w% of the EDB, in accordance with values reported in the literature^(3,6,7). Photopolymerization was carried out under laminate exposure, and the C=C bonds of the acrylate were monitored by FTIR at 1635 cm^{-1} .

Table 1. Final conversions of TMPETA achieved under different LEDs using photocatalyst systems based on Ni(II) complexes (PC/Iod or Ph-Br/EDB).

Entry	PC	Additives	Conv. (%)	LED (nm)
1	Ni(II)-dppz	Iod/EDB	72	365
2	Ni(II)-dppz	Iod/EDB	66	390-405
3	Ni(II)-dppz	Iod/EDB	11	420
4	Ni(II)-Ph	Iod/EDB	72	365
5	Ni(II)-Ph	Iod/EDB	50	390-405
6	Ni(II)-Ph	Iod/EDB	0	420
7	Ni(II)-dppz	Ph-Br/EDB	59	365
8	Ni(II)-dppz	Ph-Br/EDB	31	390-405
9	Ni(II)-dppz	Ph-Br/EDB	4	420
10	Ni(II)-Ph	Ph-Br/EDB	60	365
11	Ni(II)-Ph	Ph-Br/EDB	0	390-405
12	Ni(II)-Ph	Ph-Br/EDB	0	420
13	-	Iod/EDB	50	365
14	-	Iod/EDB	40	390-405
15	-	Iod/EDB	0	420
16	-	Ph-Br/EDB	40	365
17	-	Ph-Br/EDB	0	390-405
18	-	Ph-Br/EDB	0	420

Initially, the photoinitiating system Ni/Iod/EDB was evaluated under different LED irradiation conditions. In entries 1–3 (Table 1), TMPETA achieved final conversions under all tested LEDs, with **Ni(II)-dppz** displaying good catalytic activity, particularly under LED@365 nm and LED@390–405 nm (Figure 14). Similarly, **Ni(II)-Ph** led to final conversions under most conditions (entries 4–6, Table 1); however, no polymer formation was observed under LED@420 nm (Figure 15). Regarding the blank experiment (Iod/EDB), entries 13–15 (Table 1) demonstrated that in the absence of a photocatalyst, the photopolymerization resulted in low or no monomer conversion.

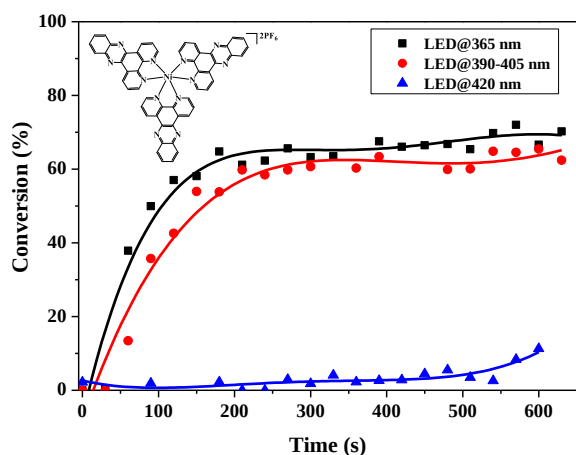


Figure 14. Conversion of TMPETA and irradiation time upon exposure to different LEDs (at 365, 390-405 and 420 nm) in laminate, using **Ni(II)-dppz**/Iod/EDB.

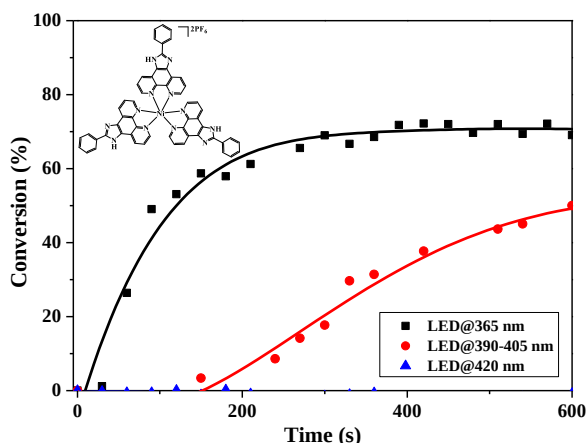


Figure 15. Conversion of TMPETA and irradiation time upon exposure to different LEDs (at 365, 390-405 and 420 nm) in laminate, using **Ni(II)-Ph**/Iod/EDB.

To explore the effect of different additives, phenacyl bromide (an electron acceptor) was evaluated (Table 1, Figures 16 and 17). For **Ni(II)-dppz**, the highest monomer conversion was achieved under LED@365 nm irradiation (entry 7, Table 1), while lower conversions, ranging from 4% to 31%, were observed under other light sources (entries 8 and 9, Table 1, Figure 16).

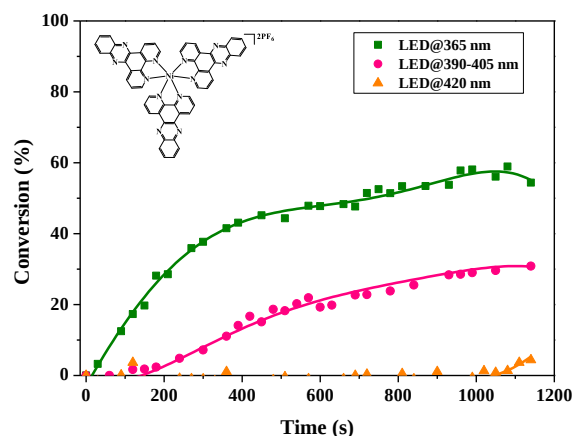


Figure 16. Conversion of TMPETA and irradiation time upon exposure to different LEDs (at 365, 390-405 and 420 nm) in laminate, using **Ni(II)-dppz**/Ph-Br/EDB.

For **Ni(II)-Ph**, a final conversion of 60% was obtained only under LED@365 nm (entry 10, Table 1, Figure 17). These results indicate that the Ni(II) complexes combined with Ph-Br and EDB exhibit catalytic activity under LED@365 nm. In the blank experiment (Ph-Br/EDB), only a low conversion was observed under LED@365 nm, and no conversion occurred with the other irradiation sources (entries 16–18, Table 1).

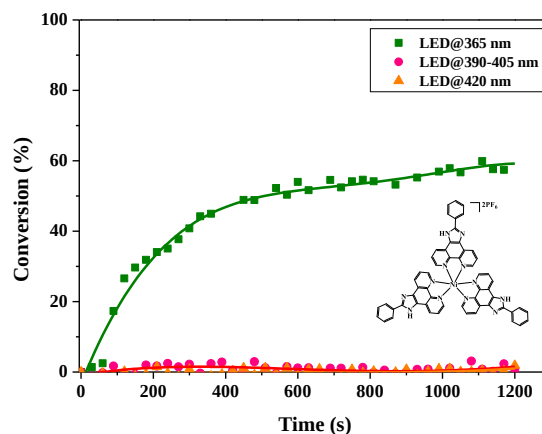


Figure 17. Conversion of TMPETA and irradiation time upon exposure to different LEDs (at 365, 390-405 and 420 nm) in laminate, using **Ni(II)-Ph**/Ph-Br/EDB.

The photopolymerization profiles of **Ni(II)-dppz** and **Ni(II)-Ph** are compared in Figures 18 and 19. **Ni(II)-dppz** showed enhanced performance compared to **Ni(II)-Ph** under all tested LED wavelengths and additive conditions. These findings can be attributed to the absorption and photochemical properties of the photocatalysts. **Ni(II)-dppz** exhibited higher absorption and emission overlap with the tested LEDs compared to **Ni(II)-Ph**.

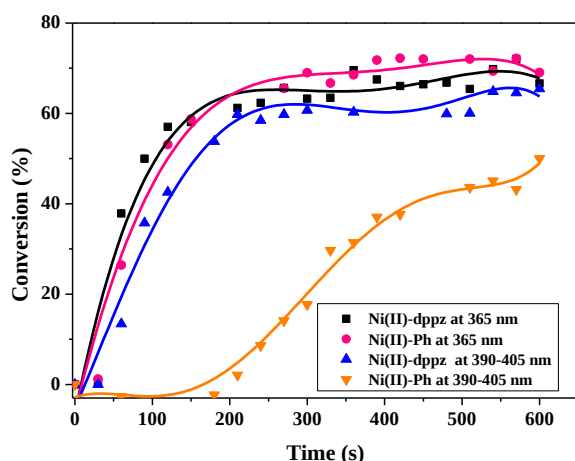


Figure 18. Conversion of TMPETA and irradiation time upon exposure to different LEDs (at 365 and 390-405 nm) in laminate, using Ni/Iod/EDB.

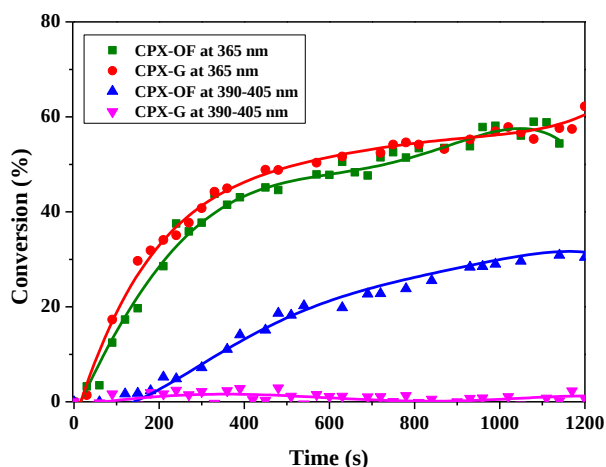


Figure 19. Conversion of TMPETA and irradiation time upon exposure to different LEDs (at 365 and 390-405 nm) in laminate, using Ni/Ph-Br/EDB.

Conclusions

The Ni(II) complexes (**Ni(II)-dppz** and **Ni(II)-Ph**) were successfully synthesized and fully characterized using various spectroscopic techniques. **Ni(II)-dppz** exhibited superior absorption and fluorescence properties compared to **Ni(II)-Ph**. In the photopolymerization experiments, the most effective and sustainable irradiation sources were LED@365 nm and LED@390–405 nm, owing to the higher absorption of the photocatalysts at these wavelengths. **Ni(II)-dppz** demonstrated better catalytic performance, achieving significant monomer conversion even under LED@420 nm. Therefore, the Ni(II) complexes were good photocatalysts for the free radical photopolymerization of TMPETA.

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