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Exploiting High-Performance Novel Ni^{II} Complexes with NHC Ligands as Photocatalysts for Advancing Photopolymerization and 3D Printing

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The use of organometallic complexes as photocatalysts (PCs) in photoredox catalysis has unveiled immense potential in radical photopolymerization. This is largely due to the dynamic interactions between the metal and ligand, with electronic transitions often occurring in the near UV/visible range.[1,2] New high-performance photocatalysts based on metal structures are continuously being developed for polymerization, but the challenge lies in balancing cost-effectiveness with performance. In this context, two novel Ni^{II} complexes, NiC1 and NiC2, were synthesized using NHC ligands (py-mesetilimidazole and ph-mesetilimidazole, respectively). These new complexes were characterized by FTIR, UV-Vis and ^{1}H NMR spectroscopy, elemental analysis, cyclic voltammetry, and mass spectrometry. NiC1 and NiC2 were evaluated in photoinitiating system for the Free Radical Photopolymerization of Ethoxylated (3) Trimethylolpropane Triacrylate (TMPETA) under violet light. This system employed three components: PCs, di-tert-butyl-diphenyl iodonium hexafluorophosphate (Iod) and ethyl dimethylaminobenzoate (EDB). Their weight content ratios in the monomer were 0.1%/1%/1%, 0.2%/2%/2%, and 0.2%/1%/1% w/w/w, respectively. The photochemical properties of NiC1 and NiC2 were investigated in CH_2Cl_2 at room temperature. These Ni^{II} complexes exhibited greater intensity and longer lifetimes compared to similar Ni^{II} complexes reported in the literature. The lifetimes were 3.8 ns and 9.1 ns for NiC1 and NiC2, respectively. The designed nickel complexes demonstrated good photoinitiation abilities. NiC2 exhibited the highest monomer conversion (> 80% at 300s) under air and in laminate, and it was investigated in the on-off process under violet light irradiation, demonstrating the efficiency of the system in reactivating the polymerization process. Oxidative and reductive pathway mechanisms were proposed based on free energy calculations, steady-state photolysis, fluorescence quenching, and electron spin resonance spin trapping experiments. The best system was successfully applied in 3D printing, generating 3D patters with smooth surfaces and good spatial resolutions within a very short writing time (Figure 1).

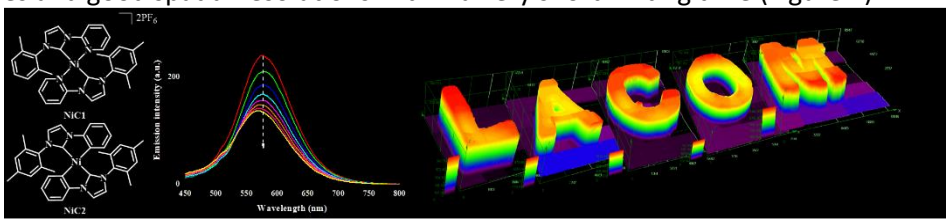

Figure 1. Investigation of the Performance and Properties of Novel Ni^{II} Complexes as Photocatalysts in Free Radical Photopolymerization (FRP) and 3D Printing.

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