

ABSTRACT

The thesis entitled, “*Design and Synthesis of Phosphate-, Amide- and Dye-linked Functional Porous Organic Polymers for Catalysis and Iodine Uptake Applications*” is divided into four chapters.

In **Chapter 1**, a concise overview is provided, outlining the pertinent topics addressed in this thesis. These include discussions on POPs, functional POPs, and their diverse applications across fields such as loading nanoparticles onto POPs for their use as heterogeneous catalysts, photocatalysts, pollutant removal, along with an exploration of the scope covered in the current study. **Chapter 2A** of the thesis focuses on the loading of Ag and Ru nanoparticles onto the porous organic polymer **OPN-4**. The resulting metal nanoparticle-loaded **OPN-4**, referred to as **Ag@OPN-4** and **Ru@OPN-4**, served as heterogeneous catalysts. **Ag@OPN-4** demonstrated effective use as a heterogeneous catalyst in the reduction of nitroarene derivatives, while **Ru@OPN-4** acted as a heterogeneous catalyst in the oxidation of benzyl alcohol derivatives. Following the completion of the reactions, both **Ag@OPN-4** and **Ru@OPN-4** were successfully removed from the reaction mixture and reused for up to five cycles. *Ref: ChemNanoMat., 2023, 9, e202300088.* **Chapter 2B** of the thesis focuses on the synthesis of a novel porous polymer, **OPN-5** and the incorporation of Pd nanoparticles onto two porous organic polymers, namely **OPN-4** and **OPN-5**. The resulting metal nanoparticle-loaded materials, designated as **Pd@OPN-4** and **Pd@OPN-5**, act as heterogeneous catalysts. Both **Pd@OPN-4** and **Pd@OPN-5** exhibited effective performance as heterogeneous catalysts in the Suzuki-Miyaura cross-coupling reactions, resulting in excellent yields. Additionally, **Pd@OPN-4** was employed as a heterogeneous catalyst in the Stille cross-coupling reaction, which also demonstrated excellent yields. Following the completion of the reactions, both **Pd@OPN-4** and **Pd@OPN-5** were efficiently removed from the reaction mixture and reused up to five cycles. *Ref: ACS Appl. Nano Mater. 2023, 6, 15002-15011.* **Chapter 3A** of the thesis is dedicated to the synthesis of three xanthene dyes, namely fluorescein, eosin yellow, and erythrosine blue-based porous organic polymers (**F-POP**, **EY-POP**, and **EB-POP**). These dye-based porous organic polymers function as heterogeneous photocatalysts. In the presence of light, the dye-based polymers generated reactive oxygen species (ROS), specifically the superoxide radical anion. This radical anion actively participated in the oxidative hydroxylation of phenylboronic acids to produce phenols at room temperature, consistently yielding good to excellent isolated yields (up to 78% for **EB-POP**). Additionally, these metal-free photocatalysts demonstrated efficient activity in generating biologically active 1,3-oxathiolane-2-thiones from styrene, achieving a 75% yield for **EB-POP**. *Ref: ACS Appl. Nano Mater., 2024, 7, 529-538.* **Chapter 3B** of the thesis is devoted to the creation of dye-based porous organic polymers, specifically **RB-POP** derived from rose bengal and **Ph-POP** from phenolphthalein. These dye-infused porous organic polymers served as heterogeneous photocatalysts. In the presence of light, these polymers generate reactive oxygen species (ROS). **RB-POP**, in particular, exhibited remarkable catalytic activities, demonstrating high efficiency in the selective oxidation of thioanisole to methyl phenyl sulfoxide (achieving up to a 98% isolated yield within 4-10 hours) and the green synthesis of benzimidazoles (with yields reaching up to 99% within 1-2 hours). Furthermore, **RB-POP** showcased impressive recycling capabilities, maintaining good photoactivity over five cycles. Overall, these findings underscored high thermal stability, robust visible light absorption capacity, and recyclability of our dye-incorporated nanoporous organic polymers. *Ref: Manuscript submitted.* **Chapter 4A** of the thesis concentrates on crafting three innovative amide-linked porous organic polymers (POPs), namely **CD-POP**, **PD-POP**, and **BD-POP**. These polymers contain a higher number of heteroatoms, enabling effective binding of iodine in both vapor and solution phases. **PD-POP**, in particular, exhibited an iodine uptake capacity of 3.53 g/g in the vapor phase and 297 mg/g in the solution phase. The adsorbed iodine was also easily removed from the polymer, and these polymers exhibited the ability to be reused up to five times without experiencing any significant loss in iodine uptake capacity. *Ref: ACS Appl. Nano Mater., 2024, 7, 1797-1803.*

Chapter 4B of the thesis is dedicated to the development of innovative phosphate-based porous organic polymers (POPs), specifically **AZO-POP-P**, **OPN-3**, **OPN-4**, and **OPN-5**. These polymers feature an increased number of heteroatoms—nitrogen, oxygen, and phosphorous—facilitating the effective binding of iodine. The chapter delved into the adsorption of iodine, whether in its molecular iodine or polyiodide state, by the polymers, elucidating the specific binding sites on the polymer. Notably, **AZO-POP-P** showcased an iodine uptake capacity of 3.56 g/g in the vapor phase. The polymers allowed for easy removal of adsorbed iodine, and these materials exhibited the capability of being reused up to five times without any significant loss in iodine uptake capacity. *Ref: Manuscript submitted.*

Keywords: porous organic polymers, nanoparticles, heterogeneous catalysis, cross coupling reactions, xanthene dyes, photocatalysis, reactive oxygen species, amide-linkage, iodine uptake.