



MSc Departmental Seminar 6001

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Thursday, July 4, 2024 at 1:00 p.m. (Room: CSF-1302)

Title: Development of Iron-based Compounds as Effective Catalysts for Lactide Polymerization and Redox-regulated Molecular Tweezers

Iron (Fe) is a first-row transition metal and the fourth most abundant element in the Earth's crust. The oxidation states of Fe can be varied from -2 to +6,¹ making it redox-tunable for various synthetic and material purposes. Fe in low oxidation states is nucleophilic, but in high oxidation states is switched to show electrophilicity and Lewis acidity. In the field of catalysis, iron-based catalysts are advantageous owing to their non-toxicity, low costs, and high abundance. In recent years, the synthesis of polylactide (PLA), a class of biodegradable and environmentally benign polymers, has been actively pursued through the iron-catalyzed approach to address the increasing concerns about the global plastic waste problem.² Iron complexes with tetradentate substituted amino-bis (phenolate) ligands have been previously reported as a type of air stable catalysts that exhibit good performance in various polymerization reactions; for example, the co-polymerization of CO₂ and propylene oxide.^{3,4} Inspired by these findings, the first project of this MSc work was focused on studying the catalytic activities of these Fe complexes in the ring-opening polymerization (ROP) of *rac*-lactide (LA) in propylene oxide. Experimental results showed a high conversion of LA to PLA. Important factors, such as temperature, catalyst loading, and co-catalyst effects, were assessed to shed light on their detailed catalytic mechanisms.

Organoiron species possess electrochemical redox activities that can be applied to the design and synthesis of functional molecular materials. Among them, ferrocene (Fc) is a popular molecular building block that has found wide application in biology and materials science.⁵ In the second project of this MSc work, a novel class of ferrocene-hinged molecular tweezers was designed and synthesized. These compounds possess a donor–Fc–donor architecture, with two electron-donating 1,4-dithiafulvenyl (DTF) groups incorporated as end groups. The molecular structural and conformational properties of these novel ferrocene derivatives were investigated by single-crystal X-ray diffraction analysis in conjunction with density functional theory (DFT) calculations and molecular dynamics (MD) simulations. The redox activities of these compounds were examined by cyclic voltammetry (CV). The possibility of these compounds to form supramolecular host-guest assemblies with cyclodextrins (β - and γ -CDs) in solution were evaluated by CV titration methods. Overall, our studies revealed their fascinating potential in redox-regulated optoelectronic molecular devices.

References:

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- (2) Driscoll, O. J.; Leung, C. K. C.; Mahon, M. F.; McKeown, P.; Jones, M. D. *Eur. J. Inorg. Chem.* **2018**, *47*, 5129–5135.

- (3) Hasan, K.; Fowler, C.; Kwong, P.; Crane, A. K.; Collins, J. L.; Kozak, C. M. *Dalton Trans.* **2008**, 22, 2991–2998.
- (4) Andrea, K. A.; Butler, E. D.; Brown, T. R.; Anderson, T. S.; Jagota, D.; Rose, C.; Lee, E. M.; Goulding, S. D.; Murphy, J. N.; Kerton, F. M.; Kozak, C. M. *Inorg. Chem.* **2019**, 58, 11231–11240.
- (5) Sarhan, A. A. O.; Izumi, T. *J. Organomet. Chem.* **2003**, 675, 1–12.