

MASTER'S THESIS

Design, Synthesis and Characterization of Phenanthroline-Based [n]Rotaxanes for Self-Sorting and Metal Ion Sensing

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ABSTRACT

Mechanically Interlocked Molecules are of significant interest to the research community as they provide the starting point to generate “machines” at the molecular level. Their significance was highlighted in the 2016 Nobel prize in chemistry, which was awarded for the “design and synthesis of molecular machines.” Particularly rotaxanes are quintessential examples of interlocked structures and give rise to a host of compounds with enhanced properties. This thesis describes several studies on the development of rotaxanes.

Chapter 1 introduces the background chemistry of supramolecules and mechanically interlocked structures, specifically $[n]$ rotaxanes i.e. [1], [2], [3] and oligorotaxanes. An overview of these rotaxanes is provided, discussing their general structures, synthetic procedures, types of intercomponent interactions and potential applications, particularly for sensing of various analytes and self-sorting into thermodynamic major products. In chapter 2, we report a new class of phenanthroline-based anthracene stoppered bistable [2] and [3]rotaxanes with self-sorting and cargo-conjugation properties, namely **4O-[2]**, **5O-[2]**, **4O-[3]**, **5O-[3]**, **4O-[2]-DMAD** and **5O-[2]-DMAD**. The [2]rotaxanes **4O-[2]** and **5O-[2]** and their respective adducts with dimethyl acetylenedicarboxylate **4O-[2]-DMAD** and **5O-[2]-DMAD** showed self-sorting ability, with the phenanthroline-based macrocycles forming on the dialkylammonium recognition site closest to the anthracene stopper on the thread. This was revealed by 2D NMR and attributed to intercomponent π -stacking interactions between the anthracene stopper and phenanthroline macrocycle, as seen in the X-ray crystallographic structures of **4O-[2]**, **5O-[2]** and **4O-[3]**. The DMAD adducts of the [2]rotaxanes showcased the ability of these compounds to conjugate to a potential cargo through facile reactions. Further experiments into the self-sorting ability and macrocycle translocation of homo threaded analogues of these rotaxanes are also discussed. In chapter 3, a series of new [24]crown-8 and

[27]crown-9 [2]rotaxanes incorporating sulfur-containing crown ethers are reported, namely **Phen-N₄S₂O₂-[2]**, **Phen-N₄S₂O₃-[2]**, **Pyr-N₃S₂O₃-[2]** and **Pyr-N₃S₂O₄-[2]**; three of the rotaxanes were studied for the selective detection of Pd²⁺ over 21 other metal cations in aqueous medium. The palladium sensor **Pyr-N₃S₂O₃-[2]** shows 53-fold fluorescence turn-on enhancement to Pd²⁺. X-ray crystallographic structures are reported for **Phen-N₄S₂O₃-[2]** and **Pyr-N₃S₂O₃-[2]**, revealing key interactions including π -stacking. The rotaxanes are reduced to give their neutral analogues **Phen-N₄S₂O₂-[2]-red**, **Phen-N₄S₂O₃-[2]-red** and **Pyr-N₃S₂O₃-[2]red** which will be further oxidized to give their sulfoxide/ sulfone crown congeners for altered redox properties and chemosensor selectivity. Further experiments into the self-sorting ability of the dithia-crown macrocycles are also discussed.