Summary

Inspired by the motion in living organisms where collective action of biological molecular machines transform chemical energy into activity, artificial molecular motors are designed to have controllable motion and responsiveness to external stimuli. These molecular machines spanning from molecular motors to switches and rotaxanes, offer a spectrum of complex functions available for the development of adaptive materials at nanoscale. My research explored the dynamic potential of artificial molecular machines as they are incorporated into different soft matter environments, including liquid crystals, micelles, and vesicular membranes. The focus is on overcrowded alkene-based molecular motors known for their ability to undergo unidirectional rotation activated by light. We studied the interplay between environmental properties and the operations of molecular machines within these soft matter media. This exploration has inspired further investigation into rotaxanes, demonstrating the transmission of chiral information in liquid crystals, where macroscopic effects are induced by dynamics of nanoscale rotaxane.

Chapter 1 served as a general introduction, providing an outline of the thesis.

Chapter 2 introduce the range of overcrowded alkene-based molecular motors operation in various environments including aqueous solution, liquid crystal, and lipid membranes. The repetitive unidirectional rotary motion fuelled by light, making them versatile tools in nanotechnology. By reviewing the dynamics of molecular motors within soft matter environments, chapter 1 emphasizes the pivotal role of environmental properties in shaping the behaviour of these motors, offering insights for the rational design of adaptive materials where molecular machines interact with and respond to soft matter environments.

Chapter 3 shows the effect of environmental organization on the rotational dynamics of molecular motors, particularly within liquid crystal media encompassing both nematic and isotropic phases. Four overcrowded alkene molecular motors were designed specifically for these investigations, revealing that molecular order of liquid crystals significantly hinders motor rotation. Our investigation into motor orientation within liquid crystal media showed that motor orientation depends on the motor structure, thus explaining the differences in their rotational dynamics. This comprehension facilitates the rational design of motors to optimize their functionality. In addition, our study identified the occurrence of the trans-unstable state motors at ambient temperature within liquid crystals, as well as their rapid trans thermal helix inversion. With understanding of regulating motor rotational speed based on environmental order, more avenues emerge for practical motor applications.

In chapter 4, we further investigated the operation of molecular motors in micellar solutions formed by different surfactants. We found that the rotation of the motor was hindered by the rigid molecular structure of specific surfactants rather than the crowdedness of the micellar environment. Our findings highlight the pivotal role of molecular stiffness in dictating motor
rotational speed. Further exploration into the influence of stiffness on molecular motor operation holds promise for designing tailored motors suitable for a wide array of environments, with potential applications as stiffness probes.

Chapter 5 demonstrates how the stiffness of the membranes influences the rotational speed of molecular motors. We designed three motors capable of incorporating into various lipid membranes. Through computational modelling, we determined the orientation of these motors within the lipid bilayer, contributing to our understanding of the relationship between molecular motor rotation and the stiffness of their environmental membranes. Our findings indicate that both the stiffness and organization of membranes decelerate molecular motor rotation. With further modifying molecular motors for incorporation into living cells, this study paves the way for effectively probing the stiffness of living cells using molecular motor as a local probe. This technique, relied on UV spectroscopy and straightforward analysis, offers potential for high-throughput screening in various vesicle types and polymer systems.

Chapter 6 extend our research scope to rotaxane-based molecular machines, building upon the insights gained from previous chapters on how environmental factors influence motor operation. Our focus expands to rotaxanes where translational motion of the macrocyclic component drives the system, distinct from the rotational motion observed in overcrowded alkene-based molecular motors. This chapter explores the chirality expression of rotaxanes and their ability to modulate liquid crystal chirality. We demonstrated that the translocation of the macrocyclic component along the thread of rotaxane molecules determines the chirality expression of the chiral center on the thread, further influencing the chirality of the liquid crystal environment. This chapter shows the broader implications of the interplay between molecular machines and their environment, highlighting the amplification of microscopic movement of the molecular machines into macroscopic-scale function of liquid crystals.

Chapter 7 explores deeper into the dynamic behaviour of rotaxanes in liquid crystal, with further focus on molecular structures containing two opposite chirality centers on the rotaxane thread. The translocation of the macrocyclic component along the thread induces opposite chirality expression in the rotaxane molecules, adding higher degree of complexity to the system when coupled with liquid crystals. This study successfully achieved the inversion of the handedness of chiral supramolecular helices induced by rotaxane chirality. This allow us to show the macroscopic effect on liquid crystals manipulating by rotaxane. By modifying rotaxanes to contain two chiral centers in this chapter, we were able to show the translation of molecular-scale translocational motion into macroscopic-scale spiral motion. Additionally, this directional motion is shown to effectively move nanoparticles within the system.

From overcrowded alkene-based molecular motors to rotaxanes, this thesis elucidates the relationship between environmental factors and motor operation. This understanding not only facilitates the rational design of molecular machines but also contributes to the development of functional systems. As we move forward, the dynamic interplay between molecular machines and their soft matter environments will continue to inspire groundbreaking discoveries and transformative applications.