Chapter 1

General Introduction

Elegant natural processes and phenomena triggered by light are widespread in daily life. For example, photoisomerization of retinal in the eyes enables vision so that the colours of nature can be perceived and appreciated. These natural phenomena hold tremendous inspiration for humans to develop functional photoactive materials and systems that serve in not only fundamental scientific studies but technological applications as well. This thesis is devoted to the study of two such material systems: organic solar cells and light-driven molecular motors, which are among the most advanced photoactive artificial material systems.

This chapter begins with a brief introduction of light-responsive artificial material systems, with organic solar cells and molecular motors as the representative systems. Then, photophysical and photochemical phenomena, the keys to this thesis, are discussed. Finally, the research goals and objectives of this thesis are formulated, and the methodology, main findings and scope of this thesis are summarized.
1.1. Introduction

Light-responsive artificial materials and devices are highly desired for scientific and technological applications. In state-of-the-art artificial material systems, the use of light enables precise spatial and temporal control of local excitations in a non-invasive way. In recent decades, research on the light-responsive artificial materials and devices has progressed nature-inspired blueprints towards scientific endeavours and more applicative efforts. A multitude of artificial light-responsive materials and devices have been developed, such as solar cells, photocatalytic water-splitting cells, light-driven molecular motors, light-responsive shape-changing polymers, and light-guided nanovehicles. This thesis is devoted to artificial material systems that convert light into electricity and use light to power molecular motors.

Organic materials are formed by organic compounds and offer numerous advantages, such as good biocompatibility, high synthetic versatility and relative ease of functionalisation. A significant class of organic materials is a material based on extended π-conjugated systems. This type of organic material exhibits semiconducting properties similar to inorganic semiconductor materials, such as silicon and gallium arsenide. It was first discovered in 1977 by A. J. Heeger, A. G. MacDiarmid and H. Shirakawa in their study of halogenated polyacetylene. Since this discovery, which was recognized by a Nobel Prize in Chemistry in 2000, π-conjugated organic materials have attracted great attention for the development and production of the next generation of electronics, known as organic electronics. Significant advances have been achieved with the successful products of organic optoelectronic devices, including, most notably, organic light-emitting diodes (OLEDs) and, most relevant to this thesis, organic solar cells (OSCs; Figure 1.1a). Recent progress in material design and device architectures has enhanced the power conversion efficiency (PCE) of most advanced OSCs to an impressive 20%.

Inspired by this success, scientists have turned their attention to the oldest OSC design, which is based on a single-material active layer and is analogous to silicon solar panels. However, the charge generation process in such devices is not well-understood and remains an open question to be addressed for the further development and optimisation of single-material OSCs. In this thesis, the charge generation process in single-material OSCs is studied using a combination of time-resolved optical spectroscopy, precise sample fabrication and kinetic Monte Carlo (KMC) simulations.
Figure 1.1. Two examples of light-responsive devices studied in this thesis. (a) Illustration of a typical organic solar cell (OSC). Sunlight transmitted to the substrate and transparent electrode excites the organic materials in which the charges are produced. The charges are then collected at the electrodes to generate photocurrent. The lower image shows Heliatek's OSC modules integrated on a building’s façade. Image credit: SEPOMO (https://www.sepomo.eu). (b) Schematic representation of a light-driven molecular motor based on overcrowded alkene. The motor absorbs light to produce rotary motion in which the rotor rotates around the axle with respect to the stator.

In addition to the conversion of light into electricity (i.e., in OSCs), the use of light to trigger photophysical and photochemical processes in materials and systems at the nanoscale is of great interest. Considerable effort in the field of light-responsive artificial materials has been devoted to designing nanoscale machines and motors capable of producing mechanical motion in response to light. During the past three decades, a variety of artificial light-driven systems has been developed, such as molecular switches\textsuperscript{25–27}, molecular rotors\textsuperscript{28–30} and, most relevant to this thesis, molecular motors\textsuperscript{8,9,31}. Among these artificial molecular machines, light-driven molecular motors (Figure 1.1b) are capable of producing autonomous motion in a controlled manner in response to light stimulation. These molecular motors have found numerous applications in materials science, catalysis and medicine\textsuperscript{8}. The scientific value of such artificial molecular motors was recognized in 2016 by the Nobel Prize in Chemistry awarded to J. P. Sauvage\textsuperscript{32}, F. Stoddart\textsuperscript{33}, and B. L. Feringa\textsuperscript{34}. Molecular motors typically require excitation wavelengths in the ultraviolet (UV) or blue regions, which is not always compatible with the surrounding (bio)environment. In contrast, light in the red and near-infrared (NIR) regions offers the optimal penetration depth in living tissue and less photochemically-induced side effects.
in biological systems. Therefore, molecular motors driven by NIR light are highly desired for their potential applications. Another challenge is related to tracking the exact motor location in a complex environment with photoluminescence (PL) microscopy, which requires a dual property of the motor rotation and PL. In this thesis, the functionality of light-driven molecular motors operating under NIR light and capable of the dual property (rotation and PL) is demonstrated using steady-state and time-resolved optical spectroscopy.

1.2. Light–Matter Interaction in Organic Materials

Light is a general term for electromagnetic radiation consisting of synchronized oscillations of electric and magnetic fields. Depending on the area of interest, the scope of the definition of light can vary from a small portion of the electromagnetic spectrum that is visible to the human eye (typically 380–750 nm in wavelength) to an entire spectrum (whether visible or not). In the quantum theory of electromagnetism, the elementary particle responsible for all electromagnetic interactions is called a photon. Depending on the photon energy, light can interact with materials in different ways. For instance, microwave radiation with a frequency in the range of 900–2450 MHz induces rotations of polar molecules to produce heat; mid-infrared radiation with a frequency in the range of 10–100 THz can excite vibrational and rotational states of molecules; visible light can promote electrons to higher electronic energy levels; UV light with a frequency that reaches the ionisation potential causes damage in soft materials and biological systems.

The term “light–matter interaction” encompasses a vast array of physical phenomena, including classical to quantum physics, black holes and neutron stars to subatomic particles and biological macromolecules to nanophononics. Therefore, to narrow down this term in the scope of this thesis, the “matter” here refers specifically to organic materials consisting of \( \pi \)-conjugated systems in their chemical structures. The interaction of organic molecules with light is primarily determined by energy levels, which are either associated with the excitation of electrons to a higher energy level (electronic energy level) or movement of the atoms in the molecule (vibrational, rotational or translational energy levels).
1.2.1. Photophysical and Photochemical Processes

A convenient way to visualize the energy levels and various transitions between them in an organic molecule is via a Jablonski energy diagram (Figure 1.2). The singlet ground and excited states are denoted as \( S_0 \) and \( S_n \) (e.g. \( S_1, S_2, \) etc.), respectively. Each state of these electronic energy levels might comprise vibrational energy (sub)levels (Figure 1.2; grey lines). Apart from the singlet excited states, a molecule can be excited (e.g. via intersystem crossing) to triplet states (denoted as \( T_1, T_2, \) etc.). The singlet and triplet states are categorized in terms of the spin multiplicity \( M \) of the energy levels according to Hund’s rule: \( M = 2S + 1 \) (where \( S \) is the total spin of the molecules); \( M = 1 \) for a singlet and \( M = 3 \) for a triplet (see Reference 35 for more detail). The energy of a triplet state is smaller than that of the corresponding singlet state (e.g. \( E(T_1) < E(S_1) \)) due to the repulsive nature of the spin–spin interactions between electrons with the same spin.

A transition between two vibrational energy levels of the same electronic state is called a vibrational transition. Transitions can also occur between two different electronic states, which are usually called electronic transitions. The transitions between electronic states of the same multiplicity (e.g. \( S_1 \) to \( S_2 \)) are much more probable than those between states of different multiplicities (e.g. \( S_1 \) to \( T_1 \)). This is because an electronic transition from singlet to triplet states (or vice versa) requires a change in the spin state of an electron during the transition. Therefore, upon absorption of a photon (optical excitation), a molecule at the \( S_0 \) state is excited to its singlet excited state. This absorption process occurs on a femtosecond (\( 1 \) fs = \( 10^{-15} \) s) timescale that is too short for significant displacement of nuclei. This is the Franck–Condon (FC) principle, and the initial excited state right after optical excitation is often called the FC state. After the excitation, the molecule at the excited state relaxes to its lowest vibrational energy level by dissipating the excess excitation energy to lower-frequency vibration modes of the molecule and its surroundings (e.g. the solvent). This process is called vibrational relaxation (or thermalisation). The molecule at the high-energy excited state can also relax to a lower-energy excited state via an internal conversion (IC) process in which the two excited states have the same spin multiplicity (e.g. \( S_2 \) to \( S_1 \)). A transition between two excited states having different spin multiplicities (e.g. \( S_1 \) to \( T_1 \)) might also occur; it is called an intersystem crossing (ISC) process. In principle, this transition is highly improbable due to the requirement of the change in the spin state of the electron. However, a spin–orbit
coupling between the spin and orbit angular momenta may make it (weakly) allowed, which results in a spin flip during the transition from singlet to triplet states (or vice versa). A strong spin–orbit coupling can be facilitated by heavy metals (e.g. rhenium, iridium, platinum, etc.) in organometallic complexes.

The vibrational relaxation, IC and ISC processes occur without any emission of radiation and thus are non-radiative processes typically occurring with timescales of picoseconds (1 ps = 10^{-12} s) to tens of picoseconds. In contrast to the non-radiative processes, the emission of electromagnetic radiation upon optical excitation is referred to as PL and it is typically divided into two subcategories: fluorescence and phosphorescence. The main difference between these subcategories is that fluorescence originates from a singlet excited state, while phosphorescence occurs from a triplet excited state to the ground state. The lifetime of fluorescence, which is typically sub-nanoseconds (1 ns = 10^{-9} s) to tens of nanoseconds, is usually shorter than that of phosphorescence, which is typically microseconds (1 µs = 10^{-6} s) to sub-seconds, due to the spin-forbidden transition from the triplet excited state to the S_0 state. The exact excited state to produce PL was first described by the American spectroscopist Michael Kasha and now is known as Kasha’s rule. It is stated as: “The emitting level of a given multiplicity is the lowest excited level of that multiplicity”. As a result, PL from the S_1 (or T_1) excited state is typically observed in nearly all molecules. However, there are exceptions, such as the well-known azulene that has fluorescence from the S_2 excited state.

A molecule at the excited state may undergo other activities, such as photochemical processes (e.g. isomerization, reactions with other species (molecules or ions)) and photophysical processes (e.g. intra and inter-molecular energy transfer). In isomerization, the molecule transforms into another isomerized form following excitation, which might exhibit different physical and chemical properties than those of the original molecule. This photochemical reaction is accompanied by a significant change either in the constitution, conformation or configuration of the molecule. Therefore, the occurrence of isomerization is primarily affected by the reaction environment, such as the temperature and nature of the surroundings (e.g. the solvent). After isomerization, the isomerized form can switch back to the initial form of the molecule via another isomerization step (e.g. photochemical or thermal isomerization).
Upon light absorption, the molecule is excited to a singlet excited state (e.g. $S_2$) and undergoes vibrational relaxation (VR) to the lowest-energy vibrational level of $S_2$. The molecule further relaxes via internal conversion (IC) from the $S_2$ to $S_1$ state, which produces fluorescence (Fl). In contrast, phosphorescence (Ph) is produced from a $T_1$ triplet excited state, which is populated by intersystem crossing (ISC) from the singlet excited state (e.g. $S_1$). In an isomerization process, the molecule at the excited state transforms into an isomerized form followed by a VR process. The isomerized form can revert to the initial form of the molecule via another isomerization step.

Molecules with $\pi$-conjugated systems can (self-)assemble as building blocks to form various structures, such as one-dimensional nanostructures (e.g. nanofibres, nanowires and nanotubes$^{42,43}$), thin-films$^{44,45}$, and molecular crystals$^{46,47}$. Because molecules in these structures are densely packed, various forms of intermolecular interactions, including $\pi$–$\pi$ stacking, hydrogen bonding, van der Waals forces, dipole–dipole interactions, hydrophobic effects, and electrostatic interactions, become critical. These intermolecular interactions drive the structures to acquire novel optical and optoelectronic properties as compared to those of the building blocks. Furthermore, delocalized excitation wavefunctions (excitons) and subsequent diffusion of excitons occur in a much broader range of a few nanometres (e.g. in amorphous and polycrystalline films$^{48}$) up to hundreds of nanometres (e.g. in nanotubes$^{49-51}$ and nanofibres$^{52,53}$). This range is equivalent to a few adjacent molecules up to hundreds of adjacent molecules.
An important class of the organic solid structures formed by \( \pi \)-conjugated systems is \textit{organic semiconductors}, which exhibit intrinsic semiconducting properties similar to inorganic semiconductors, such as silicon and germanium. Unlike their inorganic counterparts that are based on strong covalent bonds, organic semiconductors are formed by molecule-based building blocks with weak intermolecular interactions (e.g. \( \pi \)–\( \pi \) stacking\textsuperscript{54,55}, hydrogen bonds\textsuperscript{56,57}, and van der Waals interactions\textsuperscript{58,59}). The consequence can be observed in their mechanical and thermodynamic properties, namely a low melting temperature, weak mechanical hardness and low photo and chemical stability. In particular, the weak intermolecular interactions in organic semiconductors also lead to a lower dielectric constant (e.g. \( \varepsilon \approx 2 - 4 \))\textsuperscript{60,61}. Consequently, the binding energy of the exciton is large, (e.g. \( E_b \approx 0.1 - 1.0 \text{ eV} \))\textsuperscript{62-64}, and thus the distance between the electron and hole approaches zero (Figure 1.3a). This type of exciton is often called a \textit{Frenkel exciton}\textsuperscript{65}.

![Figure 1.3. Illustration of typical types of excitons in organic semiconductors. (a) Frenkel excitons. (b) Intramolecular CT excitons. (c) Intermolecular CT excitons. The blue and red dots represent the electron and hole charges, respectively, with the distance \( \langle |r_e - r_h| \rangle \) depicted as the orange lines. The magenta arrow depicts the size \( a \) of the molecule. The multiple copies of electrons and holes in each figure illustrate the delocalisation of the excitons.](image)

There is another significant type of exciton called a \textit{charge-transfer (CT) exciton}, which also includes \textit{intramolecular} and \textit{intermolecular CT excitons}\textsuperscript{66,67}. In the former case, the electron and hole charges spread over two separate electron-rich and electron-poor moieties, respectively, of the molecule structure (Figure 1.3b). Therefore, the electron–hole size is comparable to the size of the molecule (Figure 1.3c). The intramolecular...
and intermolecular CT excitons are typically realized in small “push–pull” molecules\textsuperscript{68,69} and polymers having donor and acceptor units\textsuperscript{70,71}. Furthermore, the intermolecular CT exciton is often found at interfaces of different organic semiconductors\textsuperscript{72–74} (often called an interfacial CT exciton) and of polycrystalline domains with different molecular orientations\textsuperscript{23} (also called an inter-domain CT exciton).

### 1.2.2. Molecular Photon Upconversion

Generally, molecules will emit photons with an energy lower than that of the absorbed photons (Figure 1.2). The difference between the peaks of PL and absorption spectra is called a Stokes shift. If the molecules emit photons with a higher energy than the absorbed photons, the difference is called an anti-Stokes shift (Figure 1.4a). The law of energy conservation nonetheless requires the excitation energy to be higher than the PL energy. Therefore, to realize the anti-Stokes shift behaviour, materials exhibiting a two-photon absorption (2PA) or upconversion (UC) are required. In a 2PA process, the molecule is promoted to its excited state by simultaneous absorption of two photons via a “virtual” state (with a lifetime of $\tau \sim $ fs; Figure 1.4b). Therefore, this process requires relatively high excitation peak intensities ($> 10^6 \text{ W cm}^{-2}$), which are readily reachable with ultrashort lasers.

Unlike 2PA, which is mediated by the virtual state, UC relies on a real, long-lived intermediate state. In other words, the UC process can be regarded as two sequential absorption events (Figure 1.4c). This requires low excitation intensities (less than 0.1 W cm$^{-2}$) reachable with incoherent light — for instance, solar radiation\textsuperscript{75}. Therefore, this system is attractive for solar energy applications, such as solar cells\textsuperscript{3,76}, photosynthesis\textsuperscript{1,77} and photocatalysis\textsuperscript{78}. To date, two UC systems, one based on lanthanide ions and the other based on triplet–triplet annihilation (TTA), have been developed for practical use. In the latter system, the long-lived intermediate state relies on the triplet excited states with a long lifetime in the range of tens of microseconds to sub-seconds in organic materials. The TTA-based UC (TTA-UC) requires a bimolecular system consisting of two main functional components: triplet sensitizer and annihilator. The working principle of the TTA-UC system is described as follows: First, sensitizer molecules are promoted to their $T_1$ excited states via efficient ISC from excited $S_1$ states. Second, the sensitizers transfer their excitation energy to the annihilators. Third, the TTA occurs in two excited annihilators, which brings one annihilator to the $S_1$ excited state.
while the other returns to the ground state. Finally, the excited annihilator produces UC PL (UCPL) with an energy higher than that of the excitation light. By selecting the right combination of sensitizer and annihilator molecules, desirable wavelength ranges of excitation and UCPL can be obtained. For instance, a green-to-blue UC can be realized on a Pt(II)octaethylporphyrin (PtOEP) sensitizer mixed with a 9,10-diphenylanthracene (DPA) annihilator; a combination of a tetraphenyltetranaphtho[2,3]porphyrin (PtTPTNP) sensitizer and a rubrene annihilator provides a near infrared-to-yellow UC.

**Figure 1.4.** (a) Illustration of the Stokes and anti-Stokes shifts in absorption and PL spectra. (b–c) Schematic representations of energy levels involved in two-photon absorption (b) and upconversion (c). In two-photon absorption, two incident photons (green) are simultaneously excited the molecule via an ultrashort-lived “virtual” state to the S1 state, which produces PL (blue) with a higher energy than that of the incident photons. In upconversion, the excitation takes place on an electronic transition to a “real” intermediate excited state of the material. The second excitation of the material promotes it to its higher-energy excited state, which produces upconversion PL.

### 1.3. Charge Generation in Organic Semiconductors

The creation of new materials, systems and devices exhibiting one or more valuable properties is a crucial challenge in chemistry and materials science. Nowadays, organic semiconductors, including both low-weight (or small) molecules and polymers, have advanced to the core of many optoelectronic devices, such as OSCs, OLEDs and organic field-effect transistors. This advancement has been achieved because organic semiconductors allow for the design of devices with unique properties, such as mechanical flexibility, optical semi-transparency, low-cost production, and low weight.

To utilize organic semiconductors in OSCs and photodetectors as the photoactive material, the most essential step is to split the photogenerated excitons into positive and...
negative charges, which can be extracted at the respective electrodes to generate photocurrent. The photovoltaic effect in OSCs was first observed in a simple device where a single organic semiconductor layer was inserted between two metal electrodes with different work functions. Inspired by nature, well-known organic materials for photosynthesis in green plants, such as chlorophyll-a, were initially used as the photoactive layer. However, the PCE of such simple devices was extremely low (i.e. < 0.01%).

A breakthrough in the field of OSCs came in 1986 when C. W. Tang reported a new OSC design by combining two different organic semiconductors to form a heterojunction as the photoactive layer. In a heterojunction, one organic semiconductor acts as an electron-donating (donor) material and the other functions as an electron-accepting (acceptor) material. To obtain a high charge generation yield, the excitons photogenerated in one material need to diffuse towards the donor–acceptor heterojunction to dissociate into charges. This leads to a limited thickness of the photoactive layer (≪ 100 nm) due to the short exciton diffusion length of the photoactive material, which limits light absorption. The energy offset between the frontier orbitals of the two materials was suggested to be a driving force for charge generation. The resulting PCE of OSCs was therefore improved from ~0.01% to ~1%86. With further development of the device architecture, e.g. bulk heterojunction (BHJ) and newly designed materials, especially derivatives of fullerene (C₆₀), a PCE of ~5% was obtained in the early 2000s.

Figure 1.5. Illustration of typical device architectures of organic solar cells (OSCs) based on a single organic material (a), planar heterojunction (b), bulk heterojunction of donor and acceptor (c).
Initially, a large energy offset\(^1\) between the frontier orbitals of the donor and acceptor (\(\sim 0.4 \text{ eV}\)) was believed to be an essential requirement for (efficient) exciton dissociation in many donor–acceptor blends\(^84–96\). The requirement for this large offset was motivated by the exciton binding energy, which had to be overcome for charge generation. However, the large energy offset resulted in a substantial voltage loss and hindered further improvements of the device’s performance\(^73,76,97\). The maximum PCE of OSCs based on fullerene was maintained at 11–12% between 2012 and 2017\(^98–104\). At this stage, non-fullerene acceptors (NFAs) came to the spotlight to further boost the PCE of OSCs because they were capable of a broader absorption range, higher absorption coefficient in the NIR spectrum and feasible energy level tunability\(^105–107\). The latest capacity of NFAs allowed them to better match with donor polymers in frontier energy levels, and thus a negligibly small energy offset between the lowest exciton energy and the energy of the CT state\(^72,108–110\) was obtained. This small energy offset and thus the small driving force for CT led to significantly reduced voltage losses without substantially sacrificing charge generation\(^111\). These findings demonstrated that both high photovoltage and photocurrent could be obtained simultaneously in OSCs based on NFAs. To date, the PCE of OSCs based on NFAs is approaching a significant milestone of 20%\(^18–22\), which will likely be exceeded in 2022.

In parallel to BHJ-based devices, OSCs based on a single-material (or single-component OSCs) have achieved impressive progress owing to the innovation in design and synthesis of novel materials together with the advances in layer morphology control\(^3,24\). Charge generation in these devices is often based on the formation of intermediate intra and inter-molecular CT excitons\(^68,112\), at the homojunction of single \(p\)-and \(n\)-type doped organic semiconductors\(^113\) or at the interface of undoped domains with different molecular orientations and packing\(^23\). Controlling the morphology and crystallinity of the photoactive layer, such as molecular orientation and interface contacts between \(\pi\)-conjugated backbones and side units, plays a crucial role in charge generation. So far, single-material OSCs with a PCE exceeding 11% have been realized with impressive photostability and simplified device fabrication\(^114,115\). Although single-

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\(^1\) This was later defined as the energetic offset between the lowest exciton energy (optical bandgap) and the energy of the CT state (electrical bandgap) that can be obtained accurately from (sensitive) spectroscopy methods.
material OSCs have the longest history (almost half a century) among OSCs, they have been neglected for decades and remain at the very early stages of development and optimisation, unlike the well-studied BHJ OSCs. Therefore, it is essential to further improve the device performance of single-material OSCs in future research.

1.4. Light-Driven Rotary Molecular Motors

Light-driven rotary molecular motors are a unique group of photo-responsive organic materials that convert light into mechanical motion at the molecular scale in a repetitive, unidirectional manner. Although isomerization of a molecule can provide a structural change and thus mechanical motion at the nanoscale, the major challenge lies in how to control the mechanical motion such that it occurs in a unidirectional fashion. A breakthrough in the development of molecular machines came in 1999 when Feringa and coworkers reported the first prototype of a molecular motor based on overcrowded alkenes. Due to the ingenious design of overcrowded alkenes and by incorporating chirality into the chemical structure, the unidirectionality of motion was achieved with these compounds, which exhibited a repetitive 360° unidirectional rotation. To date, various families of artificial rotary molecular motors have been realized; for instance, overcrowded alkene-based motors, hemithioindigo-based motors, and imine-based motors.

In a typical overcrowded alkene-based motor (or a Feringa-type motor), the upper and lower halves (which are sometimes called the “rotor” and “stator”, respectively) are linked by a carbon–carbon double bond acting as the “axle” of the motor (Figure 1.6). Optical excitation of the motor leads to photochemical E/Z isomerization (photoisomerization, for short) where the upper half rotates relative to the lower half, leading to a new isomer. This step is often called a “power stroke” of the motor rotation cycle. Due to a substantial change in the molecular structure after photoisomerization, a bathochromic shift is often observed in the absorption spectra of the motor. The photogenerated isomer is less stable than the initial isomer due to an energetically unfavourable equatorial conformation of the methyl substituent on the stereogenic carbon. This form is often called an unstable or metastable isomer. In Feringa-type

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\footnote{E and Z are abbreviated from the German words “Entgegen” and “Zusammen”, which mean “opposite” and “together”, respectively. The E and Z configurations at each double bond are determined by the priority of the side groups and whether the highest priority groups are on the opposite or same side, respectively.}
motors, photoisomerization is a reversible process, meaning that optical excitation also induces a photochemical back reaction to form the initial stable isomer from the metastable isomer. Alternatively, the metastable isomer proceeds to a second stable isomer via a thermal helix inversion (THI). In this process, the two halves slip past each other at the fjord regions (Figure 1.6b; orange areas), completing a 180° rotation of the motor. Unlike photoisomerization, THI is not reversible and therefore enables controlled unidirectional motion of the motor. By consecutively repeating the photoisomerization and THI steps, a repetitive 360° unidirectional rotation is achieved in a Feringa-type motor. Each motor molecule can only rotate in one direction depending on the configuration (R or S) at the stereogenic centre. Inverting a motor’s chirality will cause it to reverse direction\textsuperscript{124,125}.

**Figure 1.6. Second-generation light-driven Feringa-type molecular motors.** (a) Sketch of the chemical structure of a representative molecular motor. The space between the two halves is defined as the fjord region (orange). (b) Working principle of the light-driven rotary molecular motor. Optical excitation of the stable isomer induces the formation of the metastable isomer, which thermally relaxes to the second stable isomer via a thermal helix inversion (THI) process — that is, the upper half (red) passes the lower half (blue) at the fjord region (orange). After a subsequent excitation of the second stable isomer and another THI step, the original stable isomer is recovered, and one of the halves completes a 360° rotation with respect to the other half. Note that the lower half can be symmetrical, as drawn here, making the two stable isomers (also metastable isomers) identical. However, by desymmetrising the lower half it is possible to distinguish between them. Adapted from Reference 126 with permission from the Royal Society of Chemistry.
Light-driven rotary molecular motors are classified into different categories. Based on the number of stereogenic centres, which are essential for unidirectionality, the first, second and third-generation molecular motors are defined as comprising two, one and zero stereogenic centres, respectively, in their molecular structures\(^8,123\). In the latest generation motor, unidirectionality relies on a \textit{pseudo}-asymmetric centre\(^{127}\). Although the first-generation molecular motors usually have a high quantum yield of photoisomerization (up to 85\%\(^{128}\)), they exhibit several drawbacks: i) different activation barriers for the two different photoisomerization and THI processes\(^{116}\) and ii) synthetic challenges to selectively functionalize the upper and lower halves. In contrast, symmetrical second-generation motors have identical photoisomerization and THI activation barriers and consist of distinct upper and lower halves. Therefore, they offer more opportunities to functionalize their chemical structure for the practical application of molecular motors\(^{31}\).

\textbf{Figure 1.7.} Typical structures of various generations of light-driven Feringa-type molecular motors.

\subsection*{1.4.1. Photochemical and Thermal Isomerization in Rotary Molecular Motors}

Isomerization is a fundamentally important process in molecular machines\(^{129–131}\). Light-driven rotary molecular motors rely on two alternative processes, namely photochemical and thermal isomerization. Figure 1.8 shows a general schematic representation of photoisomerization and thermal isomerization of a Feringa-type molecular motor\(^{132,133}\). In the \(S_0\) state, the energy barriers typically separate the structural configurations of the stable and metastable isomers. Upon optical excitation, the motor’s stable isomer is excited to the FC region. Fast relaxation out of the FC region towards a
conical intersection (CI\textsuperscript{i}) with the potential energy surface (PES) of the $S_0$ state is observed, typically within (a few) picoseconds in the case of second-generation molecular motors\textsuperscript{134,135}.

By employing ultrafast fluorescence UC spectroscopy, Meech and coworkers\textsuperscript{134,136} observed the coherently vibrational relaxation of the excited state on a sub-picosecond timescale. After vibrational relaxation, the vibrationally relaxed excited state underwent a multiexponential decay, which suggests multiple pathways of structural relaxation to reach the CI (or CIs). Theoretical calculations revealed that the molecular motor needed to undergo substantial torsional motion involving a twist about the double bond of the motor’s axle and a strong pyramidalisation of the central carbon atoms of the upper half\textsuperscript{132,137,138}. Furthermore, recent publications by Meech and coworkers\textsuperscript{139,140} revealed that an energy barrier on the excited-state surface of an unsubstituted first-generation motor exists, but it is absent in an unsubstituted second-generation motor. The height of this barrier decreases with increasing solvent polarity (e.g. ethanol is a highly polar solvent), which results in a shorter timescale to access the CI with the PES of the $S_0$ state. After passing through the CI, further vibrational relaxation of the $S_0$ state leads to either the formation of the metastable isomer or the decay back to the initial stable form. The former case is productive because the metastable isomer undergoes the second isomerization, THI, to complete a 180° rotation.

In most Feringa-type molecular motors, the photoisomerization step takes place on a timescale of picoseconds, which is much faster compared to the THI step (which typically takes longer than nanoseconds). Therefore, engineering the rate of THI is one of the keys to obtaining the desired motor speed\textsuperscript{141–143}. To date, rotary molecular motors with theoretical maximum speeds of a few megahertz (MHz) under optimal irradiation conditions have been obtained\textsuperscript{144,145}.

\textsuperscript{1} A conical intersection is a molecular configuration in which multiple electronic states of a molecule are degenerate.
Figure 1.8. Energy diagram and chemical structures for unidirectional rotation via repetitive photoisomerization and thermal helix inversion (THI) steps in a representative second-generation Feringa-type molecular motor. Upon optical excitation, the stable isomer is excited to its $S_1$ excited state, which relaxes towards the conical intersection (CI) with the potential energy surface (PES) of the $S_0$ state to form the metastable isomer. Heat-induced isomerization of the metastable isomer occurs, which leads to the formation of the second stable isomer to complete a 180° rotation. Subsequent excitation of the second stable isomer promotes it to the $S_1$ excited state followed by relaxation towards the second CI with the $S_0$ state PES to form the metastable isomer, which proceeds to the original stable isomer via the second THI step and thus completes a 360° rotation. Note that the lower half can be symmetrical, as drawn here, making the two stable isomers (also metastable isomers) identical. However, by desymmetrising the lower half it is possible to distinguish between them. Adapted with permission from Reference 132. Copyright 2022 American Chemical Society.

The first light-driven rotary molecular motors required UV light to trigger the photoisomerization step. The use of harmful UV light limits the practical use of molecular motors, especially in biological systems and soft materials. For this reason, much effort has been devoted to developing molecular motors that operate with lower-energy light in the visible and NIR radiation regions. Such strategies focus not only on lowering the optical bandgap of the motor molecules but also on exploiting the low-lying triplet excited states$^{146,147}$, photon UC and multiple photon absorption processes (see Reference 148 and Chapters 3 and 4). To date, numerous molecular motors responsive up to green light with direct absorption have been realized$^{120,149,150}$. 
1.5. Goals and Objectives

The research goals of this thesis are: i) to investigate a charge generation process in single-material OSCs and ii) to exploit low-energy light to enhance the photocurrent of OSCs and to drive molecular motors with localisation capabilities.

To achieve these goals, several research objectives need to be fulfilled:

1. To elucidate the high yield of exciton dissociation in single-material OSCs based on α-sexithiophene (α-6T) with different molecular orientations.

2. To exploit a TTA-UC system that is incorporated into (single-material) OSCs, enabling the harvest of sunlight in the red region for enhancing photocurrent.

3. To utilize TTA-UC for powering a rotary molecular motor with NIR light.

4. To demonstrate the functionality of the rotary molecular motor attached to a 2PA antenna under irradiation with NIR light.

5. To demonstrate dual function (rotary motion and long-lived PL) in a family of several Feringa-type molecular motors.

1.6. Methodology

To fulfill the goals and objectives of this thesis, the approach and design of experiments need to be carefully selected. The photophysical and photochemical processes in organic materials are well-suited to be studied utilising optical spectroscopies. With the simplest UV/Vis/NIR absorption and PL spectroscopies, a considerable amount of information about the optical properties of organic materials, such as absorption and PL peaks, redshifts and blueshifts in the spectra, optical bandgaps, Stokes shifts, and PL quantum yields, can be obtained. The dynamics of different photophysical and photochemical processes, such as excited-state relaxation, PL and photoisomerization, can be obtained from time-resolved PL and transient absorption spectroscopies. Therefore, in this thesis, experimental approaches based on steady-state absorption and PL spectroscopies together with time-resolved spectroscopies are used. Details of the fundamental working principle of the time-resolved PL and transient absorption spectroscopies can be found in References 151–153 and References 154–156, respectively. Detailed descriptions of the experimental setups and sample preparations...
are presented in the Samples and Methods (or Experimental Methods) sections of each chapter.

To support the experimental results and obtain further insight into the photophysical and photochemical processes, simulation and theoretical calculations are also performed. Among them, KMC modelling\textsuperscript{157,158} is a common computational approach for non-equilibrium systems to study properties such as the diffusion of particles, chemical reactions, and crystal growth.

1.7. **Main Findings and Scope**

The main findings of this thesis are briefly described as follows:

- A high exciton dissociation efficiency in single-material OSCs originates from hundred-fold crossings of excitons of domain boundaries with different molecular orientations.
- Two molecular photon UC systems through TTA utilized for OSCs and rotary molecular motors show substantial enhancements in the photocurrent density and photogenerated motor in the metastable state, respectively.
- A rotary molecular motor equipped with a 2PA antenna is demonstrated to efficiently operate under NIR light at intensities and wavelengths compatible with \textit{in vivo} studies.
- Several Feringa-type molecular motors functionalised with triphenylamine or a BODIPY dye exhibit dual functions: rotary motion and long-lived PL. In the former motors, both functions are controlled by light with different wavelengths from the UV to NIR region.

This thesis is comprised of six chapters, including this general introduction (\textbf{Chapter 1}). \textbf{Chapter 2} is dedicated to addressing the following issue. A recent publication of Dong et al.\textsuperscript{23} has shown that single-material OSCs based on $\alpha$-6T exhibit efficient exciton dissociation at the boundaries of polycrystalline domains of standing and lying $\alpha$-6T orientations. A crucial question of the exciton-to-charge conversion remains unaddressed: What is the probability of dissociation upon a single domain boundary-crossing event? Using a combination of precise sample fabrication, time-resolved PL and KMC, it is shown that, in a model system based on $\alpha$-6T, the probability of dissociation
at the boundaries of domains with different molecular orientations is relatively low (<1%). However, the exciton crosses many boundaries on its diffusional path so that it does eventually dissociate. This finding opens up exciting possibilities for efficient exciton dissociation under conditions of a small interfacial driving force — and, therefore, a high open-circuit voltage — which the most efficient modern non-fullerene OSCs feature, but still is not well understood.

Photon UC based on TTA holds tremendous potential to exploit low-energy (e.g. red and NIR), low-intensity, incoherent (e.g. sunlight) radiation to enhance the photocurrent in OSCs or to power molecular machines. **Chapter 3** aims to examine the use of two molecular TTA-UC systems based on Pt(II)-tetraphenyl-tetrabenzoporphyrin (PtTPBP) doped in α-6T films with different molecular orientations and PtTPBP mixed with perylene in solution. In the latter system, a second-generation Feringa-type molecular motor is also attached to perylene and thereby facilitates the UC excitation energy to trigger motor rotation. The results show that the enhancements of the TTA-UC system to generate photocurrent in OSCs and to power the molecular motor are obtained under irradiation with red light. The findings of this chapter open the prospect of using molecular TTA-UC for enhancing photocurrent in OSCs as well as for driving molecular motors with low-intensity, low-energy light.

Light-driven artificial rotary molecular motors typically operate under UV or violet light, which is incompatible with most applications in soft materials and biological systems. For this reason, molecular motors functioning under red and NIR light, which benefit from an increased penetration depth into tissue and fewer potential photochemical side effects, are of great interest. **Chapter 4** demonstrates the functionality of a rotary molecular motor sensitized by a two-photon molecular antenna. First, the antenna captures two NIR photons. This is followed by the energy transfer from the antenna to the motor core that initiates motor rotation. The timescales of the energy transfer and subsequent formation of the metastable isomer are obtained using femtosecond transient absorption spectroscopy. The findings of this chapter present a gateway to future applications of sensitized molecular motors in biological settings and materials science.

Tracking the location and motion of molecular motors in a non-invasive way via PL microscopy is highly desirable to provide further insight into the performance of the motors in complex environments. The problem is that light-driven artificial rotary
molecular motors usually exhibit weak PL (quantum yield $\sim 10^{-4}$)\textsuperscript{128,135,136}, which limits the practicability of tracking the motor location. Chapters 5 and 6 report several rotary molecular motors functionalised with triphenylamine or a BODIPY dye, respectively, that exhibit the dual functions. Two different approaches to obtain multiple functions of rotation and PL are realized: i) by exploiting the two functions originated from different excited states (e.g. $S_1$ and $S_2$) in a single molecule (Chapter 5) and ii) by splitting the two functions into separate parts of the molecule (Chapter 6).

Finally, the main results and findings in this thesis are summarized.

1.8. Electronic Supporting Information

As a final remark regarding the composition of this thesis: Chapters 2, 4, 5 and 6 are based on publications, a portion of which are composed of electronic supporting information (ESI). These contain a considerable amount of data, background information and control experiments that are not essential for understanding the main objectives but demonstrate the thoroughness of the studies performed by the author(s). The large volume of ESI (approximately 50 pages for each chapter) makes it intractable to include it in this thesis. Therefore, the author decided to report here the main findings only while making the ESI available to the interested reader via a hyperlink (or a QR code) on the Abstract page of each chapter. The respective ESI sections can be downloaded free of charge, in line with the Open Science policy\textsuperscript{159}.

1.9. Personal Contribution

This thesis is a result of wide collaboration among several research groups from different institutions. The author himself performed all experiments described in this thesis, including steady-state absorption and PL spectroscopies, difference absorption spectroscopy, time-resolved PL spectroscopy, transient absorption spectroscopy, and numerical Monte Carlo simulations. The author was also directly involved in initiating and designing experiments and simulations, discussing the results and writing manuscripts for all publications. The Author Contributions sections at the end of each chapter describe the author’s contribution in greater detail.
1.10. References


