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Light-to-Energy Conversion in Organic Solar Cells and Molecular Motors

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Summary

The thesis focuses on two light-responsive systems: organic solar cells and light-driven molecular motors. In both systems, light is an input to be converted to desirable forms of energy, such as electricity in solar cells and nanoscale motion in molecular motors. The thesis provides insight into light-to-electricity conversion in organic solar cells and proposes strategic approaches to address several current limitations and challenges of light-driven artificial molecular motors in their real-life applications.

Organic solar cells have attracted extensive interest from academic and industrial communities due to attractive features, such as their light weight, mechanical flexibility, and optical semi-transparency. These impressive capacities make organic solar cells promising candidates as portable power sources which can also be integrated into the next-generation optoelectronic systems, e.g. wearable devices and energy conversion/storage systems. Furthermore, single-material organic solar cells offer excellent opportunities due to the significant advantages of considerable simplification of device fabrication and thermal stability. In organic materials, excitons — i.e. quasi-particles formed after light absorption — can dissociate into charges (free electrons and holes) when they cross boundaries of crystalline domains with different molecular orientations. **Chapter 2** demonstrated that long exciton diffusion and a large number of exciton crossings in model alpha-sexithiophene (α -6T) films contribute to the high yield of exciton-to-charge conversion. Time-resolved photoluminescence measurements and kinetic Monte Carlo simulations reveal that the single-event probability of exciton dissociation at the boundaries of crystalline domains with different molecular orientations is extremely low ($\sim 0.5\%$). However, the total share of generated charges is substantial (more than 50% of the initial excitons) as excitons cross domain boundaries hundreds of times due to their long diffusion length. This finding will ultimately contribute to the understanding of exciton-to-charge conversion in state-of-the-art organic solar cells with the small driving force of exciton dissociation.

For any type of solar cell, utilizing unharvested low-energy photons, e.g. those in the infrared spectral region, enhances the generated photocurrent and thus the power conversion efficiency. Photon upconversion that converts low-energy photons into higher-energy excitation offers exciting opportunities to exploit the light otherwise unharvested by solar cells. Particularly, photon upconversion based on triplet–triplet annihilation is attractive to the solar-cell community due to the advantage of using low-intensity excitations, which are reachable with incoherent light such as solar radiation. In the first half of **Chapter 3**, triplet–triplet annihilation-based upconversion was studied in the molecular system of a platinum porphyrin-based sensitizer (PtTPBP) and a triplet annihilator (α -6T). Thin films of α -6T doped with low-concentration (5 wt%) PtTPBP showed upconverted photoluminescence of α -6T — i.e. in the green–yellow region under excitation of PtTPBP with 635-nm red light. Exciton dissociation following the photon upconversion was shown to occur at the boundaries of crystalline domains with different molecular orientations in α -6T:PtTPBP films, similar to the neat α -6T films in Chapter 2. Manufactured organic solar cells utilizing upconversion based on α -6T:PtTPBP exhibited a significant enhancement in the photocurrent density of up to one order of magnitude as compared with the reference device without the upconversion system. These results may open up the prospect of employing triplet–triplet annihilation-based upconversion in single-material organic solar cells.

In the second half of **Chapter 3**, a rotary molecular motor powered by molecular photon upconversion based on triplet–triplet annihilation was studied. A solution mixture of PtTPBP and perylene exhibited upconverted photoluminescence of perylene — i.e. in the blue region under excitation on PtTPBP with 635-nm red light. Incorporating this upconversion system into the molecular motor by attaching perylene to the upper half of the motor, the excitation energy resulting from upconversion triggered the motor rotation. This conceptual approach opens a new route for driving molecular motors with excitation energies lower than their excited-state energies.

A two-photon absorption mechanism could be used to drive molecular motors with an even lower-energy excitation, such as near-infrared light. The problem, however, is that because of an extremely low two-photon absorption cross section in the near-infrared region, the bare motor core cannot be excited by two photons. **Chapter 4** demonstrated the functionality of a rotary molecular motor attached to a two-photon absorptive dye AF-

343 under 800-nm near-infrared light. The AF-343 dye has a large two-photon absorption cross section that is a factor of 1000 higher than the motor core and allows two-photon excitation of the dye. Ultrafast spectroscopy results revealed a high excitation energy transfer efficiency (~90%) from the AF-343 dye to the motor core for subsequent motor rotation. The large two-photon absorption cross section and efficient excitation energy transfer ensured that the molecular system could operate with low-intensity excitation by near-infrared light. The sensitized molecular motor in this chapter, together with that in Chapter 3, paves the way for future applications of molecular motors in biological settings and materials science.

For the future use of molecular motors in complex (bio)environments, monitoring the exact location of the motors in a non-invasive manner is highly desirable. Photoluminescence microscopy offers this capacity since the technique allows material systems to be monitored at length scales down to a single-molecule level. However, the very design of most of the current artificial molecular motors has been aimed at converting the photon energy into motor rotation but not photoluminescence. **Chapters 5 and 6** demonstrated a dual function of both bright photoluminescence and intrinsic rotation of molecular motors. In Chapter 5, the dual function is realized by using different excited states: motor-rotation from an S_1 state and photoluminescence from a higher-lying S_2 state. Furthermore, the motors exhibited sizeable two-photon absorption cross sections (up to ~1100 GM) under near-infrared light and therefore provided near-infrared light-driven rotation with low-intensity excitation.

In **Chapter 6**, the dual function of motor rotation and photoluminescence was realized via two separate photofunctional chromophores of a molecular system — a rotary molecular motor and an efficient photoluminescent dye. The dual function can be addressed by different excitation wavelengths of light sources in the ultraviolet–blue and green regions. In addition to the selection based on the excitation wavelength, solvent polarity could control the extent of each function. The motor–dye system exhibited brighter photoluminescence in less polar solvents and favoured motor rotation in more polar solvents. Ultrafast spectroscopy results revealed a correlation between the excited-state lifetime of the molecular system and solvent polarity, which led to the solvent dependence of the dual function. This motor–dye system, together with the motors presented in Chapter 5, lays the first stones for the foundation of artificial molecular

motors for which the nanoscale movements can be both tracked and manipulated on demand.

Overall, this thesis provides an in-depth study of molecular systems that harness light to generate electricity in organic solar cells and power the rotation of artificial molecular motors for future applications in biological settings and soft materials. The author revealed the photophysical and photochemical processes in these molecular systems using (ultrafast) spectroscopy. However, in the broader context, the work presented herein resulted from close and fruitful collaborations with chemists, material scientists, and theoretical physicists in novel molecular system design strategies. The results and findings of this thesis contribute to the understanding of exciton-to-charge conversion in organic solar-cell materials and to the prospects of using artificial molecular motors in real-world applications.