

博士論文

**Development of Nanostructured Liquid-Crystalline
Ion Conductors for Photovoltaic Applications**

(太陽電池への応用のためのナノ構造液晶イオン伝導体の開発)

ホグベリー ラルス ダニエル オスカー

1. Introduction

Renewable energy is a hot topic in today's society. Phasing out non-renewable energy sources, such as petroleum, coal and nuclear power, and transition into an energy system based on renewable energy is one of the greatest challenges in present time. The largest renewable energy source available is the sun, and harvesting only a fraction of its energy would be more than enough to meet today's, and future energy needs of the world. Solar cells are devices used to directly convert sunlight into electricity. However, it is difficult to achieve sufficient energy production at a reasonable cost in order to compete with cheaper fuels, such as coal. Third generation solar cells such as perovskite solar cells (PSCs) and dye-sensitized solar cells (DSSCs) have attracted a great deal of attention in recent years as lower cost alternatives. In particular, PSCs has received a lot of attention due to the rapid progress in improving device efficiency. However, the use of toxic and unstable materials limits the commercialization of PSCs. On the other hand, DSSCs are constructed from abundant non-toxic materials, and show sufficient conversion efficiency and long-term stability for commercial applications. However, DSSCs require the use of liquid organic solvent-based electrolytes in order to achieve desired performance. The potential leakage and evaporation of the electrolyte is a problem that affects the life-time of the devices. Overcoming these issues are of great importance for commercialization of DSSCs.

One approach to develop materials that overcome the limitation of liquids is to use the self-assembly of organic molecules into functional nanostructured. In particular, liquid crystals with well-defined nanopathways for the transport of ions are prospective as electrolytes in energy devices. Applying liquid crystals in DSSCs may solve the fundamental issues associated with liquid electrolytes such as leakage and evaporation. The objective of this thesis is to design and synthesize physically robust and thermally stable ion conductors based on liquid crystals. This new class of electrolytes will be applied in DSSCs, and their performance in operating devices will be evaluated.

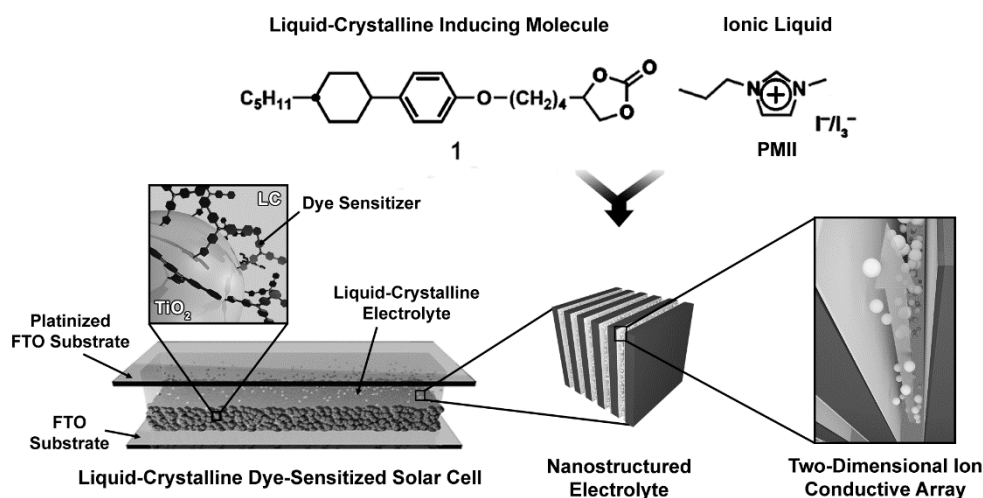


Figure 1. Conceptual image of nanostructured material consisting of molecule **1** and ionic liquid **PMII**.

2. Rod-Like Liquid Crystals as Electrolytes in Dye-Sensitized Solar Cells

The aim of this chapter is to design rod-like mesogens that show thermally stable LC phases and exhibit high ion-mobility with the aim to develop stable and durable DSSCs. With this goal in mind, a new two-component LC electrolyte, consisting of the carbonate-based mesogenic molecule **1** and the ionic liquid (IL) **PMII** (Figure 1), has been developed. The electrolyte (**1/PMII**) is composed of **1** and **PMII** (20 mol% of I₂) in a 40:60 mol % (**1**:**PMII**) ratio. The **1/PMII** mixture exhibits a layered smectic A (Sm A) LC phase from 0 to 108 °C and the IL was found to be incorporated inside the layered nanostructure. The ion conductivities were measured parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the layers. The value of σ_{\parallel} is $2.1 \times 10^{-4} \text{ S cm}^{-1}$ at 40 °C is about 4.5 times higher than the value of σ_{\perp} ($4.8 \times 10^{-5} \text{ S cm}^{-1}$). These results suggest that **1/PMII** exhibit anisotropic ion conduction in the LC state. The LC electrolyte was applied in DSSCs and the initial devices showed a power conversion efficiency (PCE) of 2.2 % at 60 °C. The PCE was improved to 3.9% at 60 °C by increasing the thickness of the TiO₂ film used as working electrode. Furthermore, three widely used dye sensitizers based on different fundamental molecular building blocks were studied in the LC-DSSCs; the indole-based **D205**, the triphenylamine-based **D35**, and the ruthenium-based **N719** (Figure 2). It was found that the type of dye sensitizer significantly affect the performance of the LC-DSSCs. The **1/PMII** devices show higher PCE when using organic dyes as compared to standard ruthenium based metal-complexes. The best PCE of 5.2 % was obtained with the indole-based dye (**D205**). In contrast, the standard ruthenium dye **N719** showed a PCE of 2.2 %. This difference was traced significantly lower photocurrent and open-circuit voltage of the **N719**-based DSSCs. It was found that the **N719**-based devices suffered from low electron density in the working electrodes, indicating problems with electron injections. Two plausible theories are proposed for the observed difference in electron density of the organic-based and metal-complex based LC-DSSCs. The self-assembled LC structure might decrease the access of the I⁻ species to reach and regenerate some of the dye molecules. This limitation is possibly mitigated in the organic dye-based devices because of the fast intermolecular charge hopping between organic dyes, which may lead to more rapid regeneration of dyes molecules not in direct contact with I⁻.

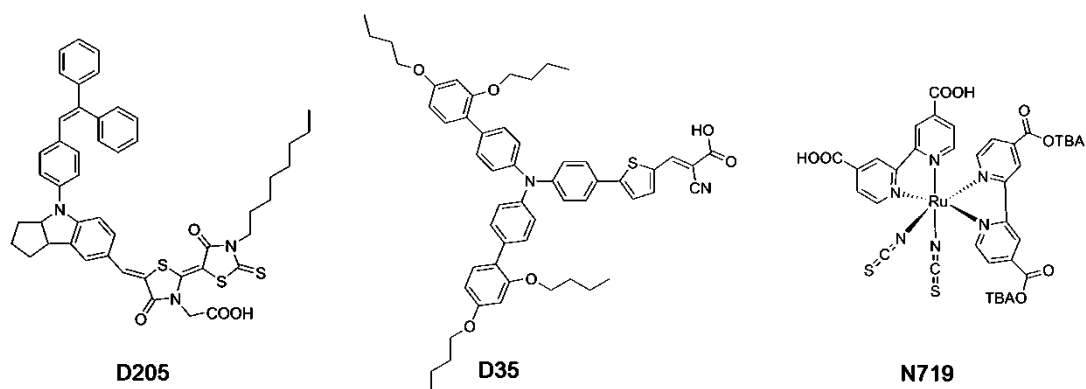


Figure 2. Molecular structures of dye sensitizers **D205**, **D35**, and **N719**.

On the other hand, it has previously been reported that ruthenium-based sensitizers suffer from a fast reductive quenching process in the presence of high concentrations of iodide. This reaction competes with the electron injection into the TiO_2 . In the case of the LC electrolyte **1/PMII**, the iodide species are located, and highly concentrated, within the confined nanostructure. The accumulation of ions in the close proximity of dye molecules that are in direct contact of I^- may promote the reductive quenching of the excited **N719** molecules. Both of these processes would as a consequence leads to a decrease in the electron injection rate of the dyes in the **1/PMII(N719)** based devices and ultimately the electron density in the TiO_2 substrate.

3. Thermal Properties of Liquid-Crystalline Electrolytes Dye-Sensitized Solar Cells

The aim in this chapter is to develop DSSCs that can operate efficiently at elevated temperatures and to evaluate the device performance as a function of temperature. In order to achieve this, solar cells based on the liquid crystal **1/PMII** have been studied as a function of temperature and compared with reference cells containing only **PMII**. The **1/PMII**-devices show an increase in power conversion efficiency (PCE) on heating from 1.0 % at 30 °C to 2.7 % at 90 °C (Figure 3a). In contrast, a decrease from 2.9 % at 30 °C to 1.5% at 90 °C was observed for the liquid **PMII**-devices. Interestingly, the **1/PMII**-DSSCs show higher PCE as compared to the IL-based device over 70 °C, even though the IL electrolyte show higher ion diffusion at this temperature. These results indicate that other factors than the mass-transport of the electrolytes play a role in the improved temperature performance of the LC-DSSC. It was found that the **1/PMII**-based cell exhibits longer TiO_2 electron life-time (τ) than the IL-based cell (Figure 3b). Furthermore, the **1/PMII** device shows a slight τ decay upon heating. However, this tendency is more pronounced for the **PMII** device. These observations suggest that unwanted electron recombination reactions issues become more significant in the IL-based cell than in the LC-based DSSC at elevated temperatures. It is proposed that the polar carbonate moieties and ionic species interact with the TiO_2 surface, driving self-organization along the electrode surface, which spontaneously induces the formation of a nanostructured insulating layer around the $\text{TiO}_2/\text{D35}$ interface. The formed layer would act as a barrier against the I_3^- species and lead to a decrease in the undesired electron recombination process.

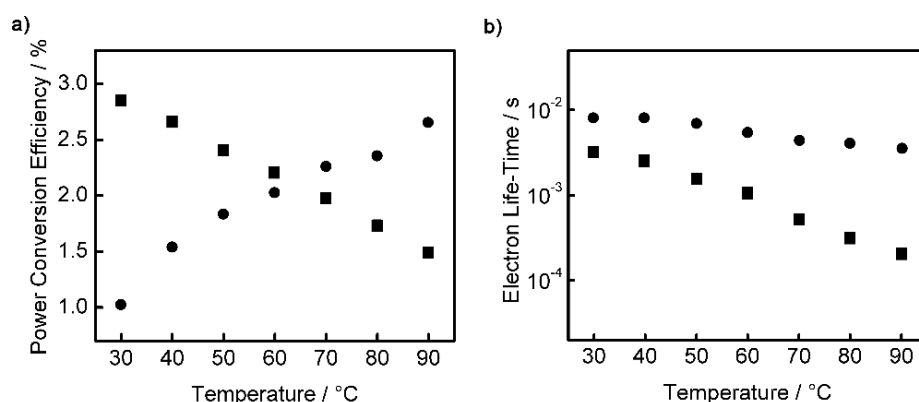


Figure 3. a). Power conversion efficiency and **b)** electron life-time as a function of temperature of a DSSCs containing **1/PMII** (circles) and **PMII** (squares).

4. Mesogens Functionalized with Oligooxyethylene Linkers for Improved Solar Cell Performance at Room Temperature

With the aim to further improve the PCE of the LC-DSSCs, a longer and more flexible oligooxyethylene spacer was introduced in molecular design of compound **2** (Figure 4a). In our initial design, the polar moieties were linked to the mesogens by non-polar alkyl spacers (compound **1**), Figure 4b. In the new design, we introduce the more flexible polar spacer with the intent to increase the fluidity of the layers in the LC nanostructures and to suppress crystallization of the materials, which is expected to lead to an increase in ion mobility. The 50:50 mol% mixture of **2** and EMII (**2/EMII**) shows a Sm A phase from below 0 to 78 °C. In contrast the alkyl-linked **1/EMII** show a crystal to Sm A phase transition at 62 °C and a melting point at 119 °C. The oligooxyethylene spacer successfully suppresses crystallization at lower temperatures. Furthermore, higher triiodide diffusion ($D_{I_3^-}$) was measured for the **2/EMII** electrolyte as compared to the alkyl-linked electrolyte **1/EMII** (Figure 4c). The **2/EMII**-DSSCs show a maximum PCE of 6.1% (average 5.8%) at 30 °C (Figure 4d). In contrast the **1/EMII**-DSSCs show a PCE of 1.6%. The oligooxyethylene linker successfully improves the PCE of the LC-based devices at lower temperatures. As temperature is increased, the device performance of the **2/EMII**-DSSCs gradually decreases. However, more than 90% of the initial PCE value (5.2%) is maintained at 60 °C. On further heating, the rate of decrease in PCE is significantly increased after the temperature reaches the isotropization point of 78 °C. This indicates that the LC state of the electrolyte is important for the stable PCE at higher temperatures. Furthermore, long-term stability tests reveal that both electrolytes show excellent stability over 1000 hours.

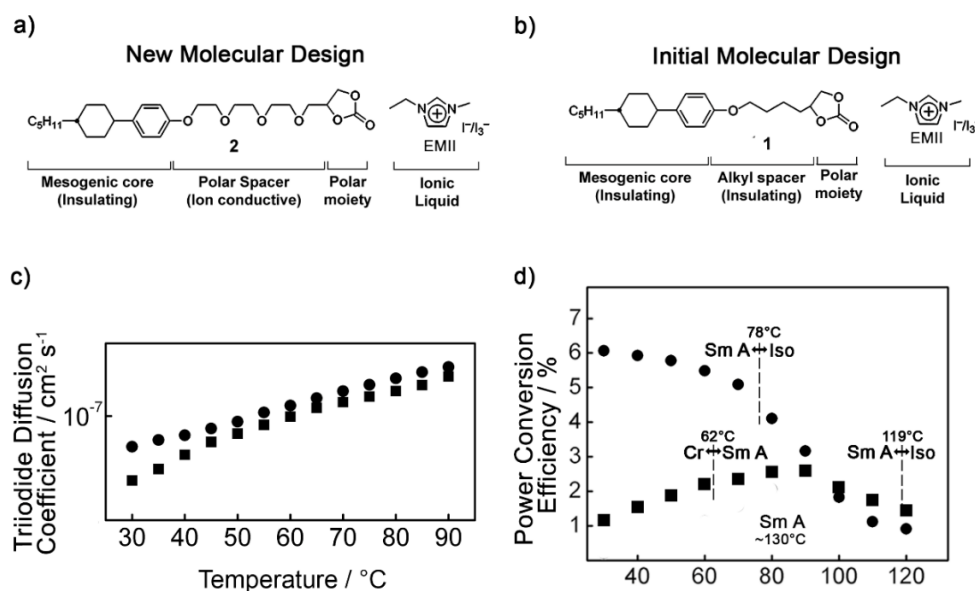


Figure 4. Molecular structure of **a)** compound **2** and **b)** compound **1**. **c)** Triiodide diffusion coefficients of electrolytes **1/EMII** (squares) and **2/EMII** (circles). **d)** Power conversion efficiency as a function of temperature of DSSCs containing **1/EMII** (squares) and **2/EMII** (circles).

5. Covalent and Non-Covalent type Liquid Crystals as Transport Materials

Throughout this thesis, LC electrolytes based on two-component liquid crystals has been developed and presented as advantageous electrolyte systems for DSSCs. In chapter 4, it was indicated that the stability of the LC phase is important in regards to stable performance at higher temperatures. However, the two-component molecular design limits the thermal stability of the LC phases due to nanosegregation through weak dipole forces. To overcome this, single component ionic liquid crystals has been designed (Figure 5), where the cyclic carbonate moiety has been replaced with an imidazolium iodide. Ionic mesogens are known to form highly stable LC phases through strong electrostatic interactions. In this chapter, DSSCs based on this new ionic single component liquid crystals has been developed with the aim to obtain DSSCs capable of operating at extreme temperatures. Furthermore, the single-component DSSCs has been compared with their two-component analogous, and the effect of the LC phase stability on photovoltaic performance of the devices were evaluated. Compound **3** show a Sm A phase from below 0 to 180 °C, significantly wider than for the two-component analogue **2/EMI**. The LC-DSSCs containing **3** show significantly lower PCE compared to the two-component **2/EMI** at lower temperature. However, as temperature reaches 90 °C, the **3**-based DSSCs show higher PCEs than the **2/EMI**-based devices, and reaches a maximum PCE of 2.4% at 120 °C. This is an improvement of the maximum operation temperature by 30 °C as compared to the **1/PMI**-DSSCs reported in chapter 3. These results can most likely be traced to the more thermally stable LC phase of **3**. The stability of the self-assembled nanostructures is apparently paramount to achieve stable device performance at elevated temperatures. Furthermore, the LC-DSSCs exhibit excellent long-term stability over 1000 hours at the operation temperature of 120 °, indicating that these LC-devices can operate long-term under these extreme conditions.

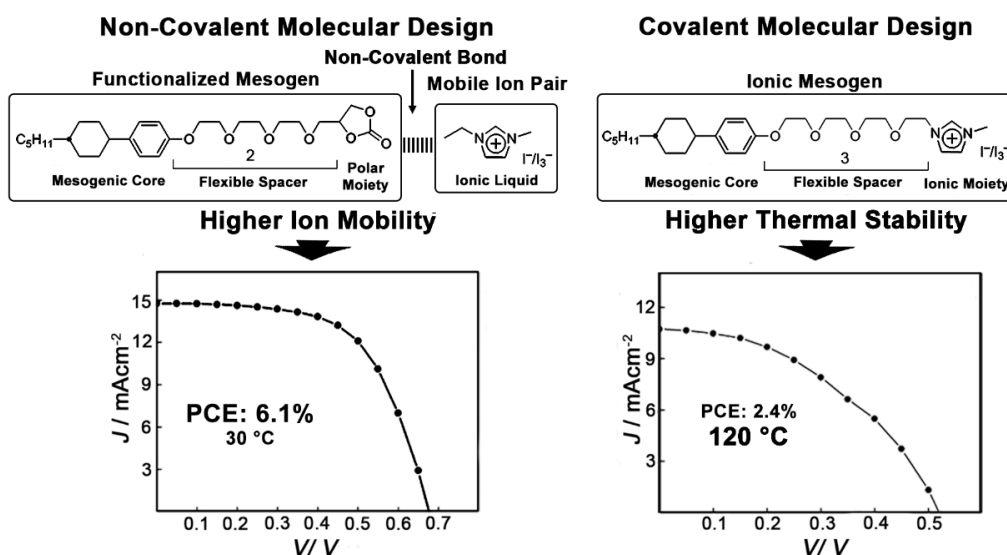


Figure 5. Molecular design of non-covalent-type liquid crystal **2** (left) and covalent-type liquid crystal **3** (right), and the power conversion efficiencies of DSSCs based on the electrolytes.

6. Conclusion

Liquid-crystalline electrolytes that show excellent physical properties and thermal stability has been developed and applied in DSSCs. DSSCs based on the LC electrolytes show better photovoltaic performance at elevated temperature as compared to liquid-based devices. This behavior is traced to the self-assembling properties of the liquid crystals. It is also found that the LC based electrolytes are more suitable to be used together with organic dye sensitizers as compared to standard ruthenium-based complexes. Furthermore, the introduction of the flexible oligooxyethylene spacer in the mesogenic molecular design between the terminal group and the mesogenic moiety significantly improves the PCE of the LC-DSSCs. The DSSCs containing the **2/EMII** electrolytes show a maximum PCE of 6.1 %, the highest PCE reported for LC-DSSCs. In contrast, covalent-type liquid crystals show excellent high temperature stability and performance. A maximum PCE value of 2.4% was obtained at 120 °C for DSSCs containing **3**, the highest max operating temperature reported for a solar cell. In addition, DSSCs based on the LC electrolytes show excellent long-term stability over 1000 hour. These LC electrolytes opens up new paths for developing durable DSSCs that can be operated under extreme conditions. Furthermore, the robustness and the flexible molecular design of liquid crystals show their potential as a new class of electrolytes that may contribute to the development of efficient and safe energy devices.

7. Acknowledgements

First and foremost, I would like express my greatest gratitude to my supervisor, Prof. Takashi Kato, for his guidance and encouragement these past years. I would also like to express my greatest gratitude to both Prof. Hiroshi Segawa and Prof. Lars Kloo for their collaboration in this project and making this thesis possible. I would like to thank Prof. Satoshi Uchida and Prof. Masafumi Yoshio for continuously teaching me and always giving me the needed support to push the research forward. Lastly, I would like to thank all the members in both Kato laboratory and Segawa laboratory for making these past 3 years very enjoyable. I would also like to acknowledge the financial support from the Japanese Government in the form of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) scholarship.

8. References

- [1] T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno, M. Funahashi, *Nat. Rev. Mater.* **2017**, 2.
- [2] Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, 110, 6595–6663.

List of Publications

1. Högberg, D.; Soberats, B.; Uchida, S.; Yoshio, M.; Kloo, L.; Segawa, H.; Kato, T. *Chem. Mater.* **2014**, 26, 6496–6502. *ACS Editor's Choice, Highlighted in ACS C&EN News. November 2014.*
2. Högberg, D.; Soberats, B.; Uchida, S.; Yoshio, M.; Kloo, L.; Segawa, H.; Kato, T. *Chem. Mater.* **2016**, 28, 6493–6500. *Selected as Journal Cover.*
3. Högberg, D.; Soberats, B.; Uchida, S.; Yoshio, M.; Kloo, L.; Segawa, H.; Kato, T. *ChemPlusChem* **2017**, 82, 834–840. *Selected as Journal Cover.*