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題目(和文)	トレガー塩基誘導体の開発とペロブスカイト型太陽電池におけるホール輸送材料としての応用
Title(English)	Development of Tröger ’ s Base Derivatives and their Application as Hole Transporting Materials in Perovskite Solar Cells
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Thesis Outline

In this thesis, the author demonstrated how Tröger's base enantiomers become efficient hole transporting materials (HTMs) in perovskite solar cells (PSCs). In order to fulfill this goal, there are two key points, namely, the design of Tröger's base derivatives and the fabrication of PSCs. The thesis was divided into seven chapters as follows.

In Chapter 1, the history and development of PSCs were briefly introduced. Most importantly, various organic HTMs and their performances in the PSCs were focused. The background and previous researches about Tröger's base derivatives were also discussed. The synthesis and chirality of Tröger's base compounds were first introduced. This was followed by the applications of these compounds, especially as HTMs.

In Chapter 2, novel Tröger's base-containing linear polymers were synthesized by the Pd-catalyzed polycondensation of 2,8-disubstituted Tröger's base monomers. These linear polymers exhibited unique optical-electrochemical properties. Polyaryleneethynylene-type polymers were typical dual color-emissive polymers with blue in the solutions and light-green in the thin solid films. In contrast, a similar phenomenon was not observed for the corresponding polyarylene-type polymers. The electrochemical properties of these polymers depended on the chemical structures. The ethynylene linker in the polymer main chain as an effective π-spacer could facilitate the oxidation process. The linear polymers containing the triphenylamine unit were more redox-active than similar polymers with the fluorene unit. However, the redox properties and solubility of these polymers proved unfit for the HTMs of PSCs.

In Chapter 3, novel Tröger's base-1,1,4,4-tetracyanobuta-1,3-diene conjugates (TB-TCBDs) were synthesized by a [2+2] cycloaddition-retroelectrocyclization click reaction. The chiral resolution of TB-TCBDs was conducted by HPLC on chiral stationary phase (CSP). The optical and electrochemical properties of these

enantiomerically pure compounds were investigated in order to understand the chiral induction and racemization of Tröger's bases. Interestingly, the two terminal aniline groups of TB-TCBDs formed a face to face parallel structure. The π-π interaction between the anilines might have forbidden the racemization of Tröger's base even in acid media. As a result, these chiral TB molecules exhibited high stability toward protonic acids.

In Chapter 4, since Tröger's base-containing linear polymers were not appropriate HTMs of PSCs, two types of carbazole and EDOT copolymers (Cbz-EDOT) were newly synthesized by the Stille coupling reaction and used as HTMs in the optimization of device fabrication conditions. Two polymers have similar structures except the connectivity pattern of the carbazole unit. Photovoltaic parameters of these devices suggested that the devices based on 2,7-Cbz-EDOT showed a higher PCE than the devices based on 3,6-Cbz-EDOT due to the linear conjugated structure of the carbazole moiety. More importantly, the relationship between the structure of HTMs and photovoltaic performances were thoroughly studied. Also, the fabrication conditions of PSCs were optimized by using 3,6-Cbz-EDOT as an HTM.

In Chapter 5, a series of hole transporting polymers were synthesized by direct arylation polymerization. High molecular weight polymers could be generated in short time with the assistance of microwave heating. All the polymers were utilized as HTMs of PSCs. In order to improve the photovoltaic performances of PSCs, dopants such as bis(trifluoromethane)sulfonimide lithium salt (Li-TFSi) and *tert*-butylpyridine (TBP) were added to the polymeric HTMs. It was revealed that both dopants were effective for the enhancement of photovoltaic properties.

In Chapter 6, three Tröger's base derivatives with the carbazole-based donor substituents at the 2,8-positions were synthesized by the Buchwald-Hartwig amination reaction. These Tröger's base racemates, (±)-TB-diphOMe, (±)-TB-Cbz-3,6-diphOMe, and (±)-TB-Cbz-2,7-diphOMe, were utilized as HTMs of PSCs. Among the three derivatives, the best photovoltaic performance was achieved for the device based on (±)-TB-Cbz-2,7-diphOMe with the PCE of 8.99%. Furthermore, the enantiomers of

TB-diphOMe and TB-Cbz-2,7-diphOMe, successfully isolated by HPLC on CSP, were examined as HTMs of PSCs. Interestingly, it was found that these enantiomers exhibit different mobility and photovoltaic properties when the rotational direction of spin-coating is changed. The highest PCE of 11.16% was achieved for the device based on (+)-TB-Cbz-2,7-diphOMe enantiomer when the HPM was spin-coated in the clockwise direction. In the clockwise direction, the positive enantiomers were more effective HTMs probably due to the suitable self-assembled thin film structures. This was the case for the negative enantiomers that showed better mobility and photovoltaic properties in PSCs when their films were formed by spin-coating in the anti-clockwise direction.

In Chapter 7, the achievements of this thesis were summarized. This thesis thoroughly investigated the optical, electrochemical, and chioptical properties of Tröger's base derivatives. It was for the first time revealed that the Tröger's base enantiomers are a new class of HTMs of PSCs.