論文の内容の要旨

Synthesis and Materials Properties of Spiro-conjugated Carbon-bridged Phenylenevinylenes

（スピロ接合型炭素架橋フェニレンビニレンの合成と物性）

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1. Introduction

Organic π-conjugated molecules have been attracting much attention because of their potential applications in optoelectronic and semiconducting materials. The properties of organic materials are largely derived from their molecular structure. Hence, the construction of new molecular backbone by molecular design enables the desired properties and opens up the new dimensional materials. Based on this concept, in my doctoral course study, I developed two new π-conjugated scaffolds. The desired materials properties is successfully achieved by the combination of functional structures, which provided the opportunities for further applications.

2. Tetrakis(benzo[*b*]furyl)ethene (TBFE): Combination of Aggregation-responsive Fluorescent Behaviors

Aggregation-responsive fluorescence is an attractive property because of their potential applications in light-emitting devices and biological probes. Aggregation-caused quenching (ACQ) and aggregation-induced emission (AIE) enable aggregation-triggered fluorescent on-off switching behavior. However, three-stage on-off-on switching only upon aggregation has not yet been achieved. Focusing on that both of them are mechanistically derived from molecular structure, I envisioned that ACQ and AIE could be integrated in one molecule through molecular design. Continued through my master and Ph.D. course studied, investigation on tetrakis(benzo[*b*]furyl)ethene (**TBFE**) revealed that this compound does show the expected properties. As obtained via hafnium-mediated McMurry coupling, the compound exhibited three-stage two-wavelength on-off-on fluorescence switching behavior. Fluorescence spectra of **TBFE** in THF/H_2O mixed solvents exhibited the on-off and off-on switching behaviors at 360 nm and 510 nm upon addition of H_2O. No observation of peak shift at 360 nm suggested ICT process, which attributes to the previous switching systems, is not involved here. Slow nonradiative decay, large and spherical aggregates in 90% H_2O suggested the three-stage switching is triggered by aggregation. This study suggested the structure-derived properties could be compatible in one molecule and encouraged the research on spiro-CPV.

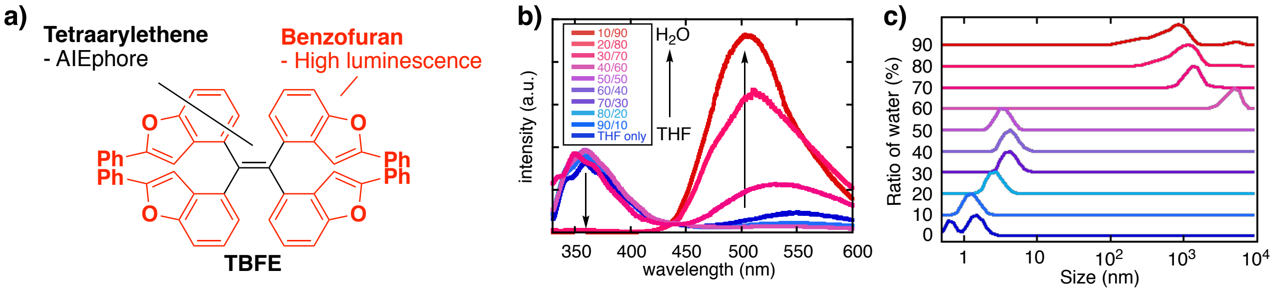

Figure 1. Fluorescence switching behavior of tetrakis(benzo[b]furyl)ethene (**TBFE**). a) Molecular design. b) Fluorescence spectra, c) size distribution in THF/H_2O mixed solvent.

3. Synthesis, Optical Resolution, and Materials Properties of Spiro-conjugated Carbon-bridged *p*-Phenylenevinylene

π-Conjugated compounds bearing spiro-linkage evokes attractive material properties because of their three dimensional structure and electronic interaction between two π-systems via spiroconjugation. Our laboratory has developed carbon-bridged oligo(*p*-phenylenevinylene)s (COPVs), designed by fixing each units of oligo(*p*-phenylenevinylene)s. Because of structural flatness and rigidity, COPVs exhibit high fluorescence quantum yields (Φ_{FL} ~1), high photo and thermal stability, and fast charge transfer through the conjugated system, which allow their applications in laser dyes and molecular wires. I noticed that the bridging carbon atom can be utilized as a spiro chiral center, and investigated synthetic feasibility of C_2-symmetric spiro-conjugated carbon-bridged *p*-phenylenevinylene (spiro-CPV), where two COPV units are connected via a spiro-linkage at the bridging carbon atom. This strategy was expected to create a novel spiro-conjugated π-backbone for circularly polarized luminescence (CPL) with high stability, and isotropic carrier transfer ability.

Spiro-CPV was found to show the properties derived from both spiro structure and COPV. Spiro-CPV (**A**) was successfully obtained via Pd-catalyzed cyclocarbonylation to afford the key ketone intermediate. The spiro backbone undergoes regioselective halogenations in excellent yields to allow further derivatizations. Small Stokes shift of **A** (64 nm) as well as COPV1 (60 nm) suggested structural rigidity of **A** upon photoexcitation. Because of its molecular chirality and rigidity, enantiomerically pure **A** exhibited CD and CPL ($|g_{abs}| = 8.4 \times 10^{-4}$, $|g_{lum}| = 6.3 \times 10^{-4}$) with high Φ_{FL} of 0.74 The investigation on molecular orbital energy levels of **A** suggested the inter-subunit electronic interaction, so-called "spiroconjugation", between two COPV units. Spiro-CPV showed high stability against thermal and photo stimuli, allowing the applications into optoelectronic device materials.

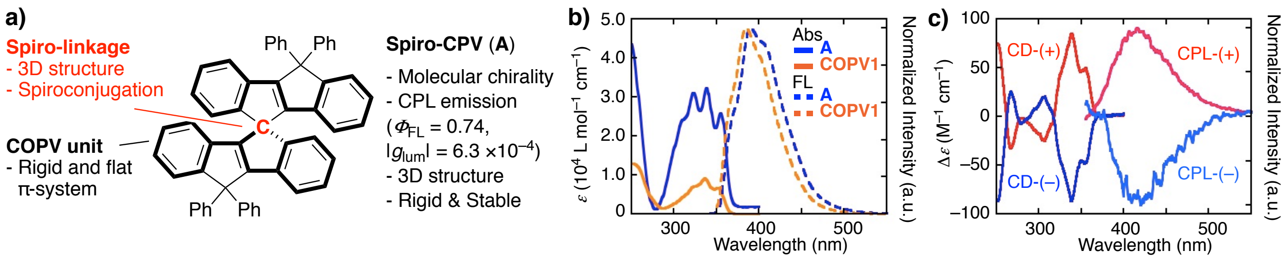

Figure 2. a) Molecular structure of spiro-CPV (**A**). b) Absorption and fluorescence, and c) CD and CPL spectra of **A** and COPV1.

4. Enhancement of Circularly Polarized Luminescence by Elongation of *π*-systems of Spiro-CPV

High radiative rate constant k_r, and hence, Φ_{FL} are important issues to be focused for the development of light-emitting applications. For example, organic dye laser requires materials possessing $k_r \geq \sim 4 \times 10^8$ s^{-1} for amplified simultaneous emission. Considering that k_r is ideally proportional to the integral of extinction coefficient ε over the absorption bands, I envisioned the π-elongation of each COPV units would improve ε to enhance k_r and Φ_{FL}. In this work, I decided to install phenyl and phenylethynyl groups on the terminals of each COPV units. For longer conjugated systems, enhanced absorption was observed in the long wavelength region. Thus, k_r and Φ_{FL} were successfully enhanced by π-elongation to achieve k_r of 4.07×10^8 s^{-1} for the phenylethynyl derivative as well as Φ_{FL} of 0.99, the highest among organic CPL materials reported thus far.

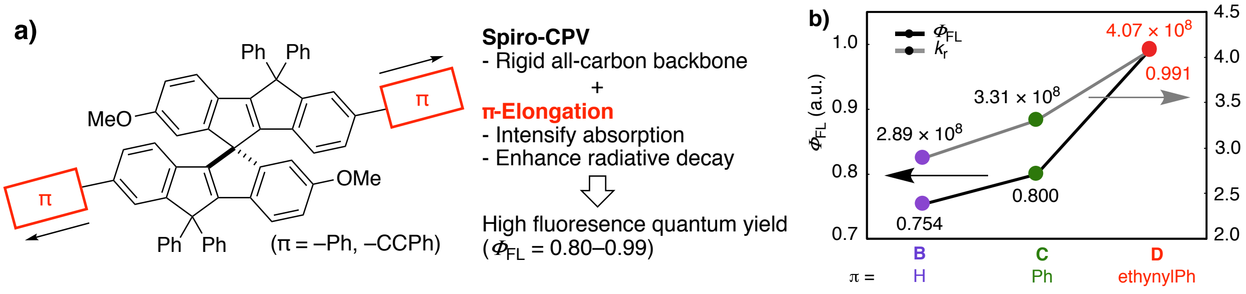

Figure 3. Elongation of COPV units in spiro-CPV. a) Concepts for molecular design. b) Enhancement of Φ_{FL} and k_r.

5. Spiro-conjugated Carbon and Heteroatom-co-bridged *p*-phenylenevinylenes: Synthesis, Materials Properties, and Solvatochromic CPL

Introduction of heteroatoms to the conjugated systems is an effective strategy for modification of molecular properties. The use of electron donating and withdrawing properties of heteroatom efficiently changes electronic structures. However, it often causes the structural reorganization upon photoexcitation. I envisioned that incorporation of heterocycles to the rigid spiro-CPV backbone would tune their electronic properties without causing the reorganization. Oxygen, nitrogen, sulfur, and sulfur dioxide were incorporated in place of a bridging carbon atom. The electronic properties were affected by the electronic effects of fused heterocycles. Especially, the SO_2-bridged one exhibited positive solvatochromic fluorescence because of the inter-subunit intramolecular charge transfer increasing the dipole moment in its excited state, as well as larger $|g_{lum}|$ than the other spiro-CPV derivatives.

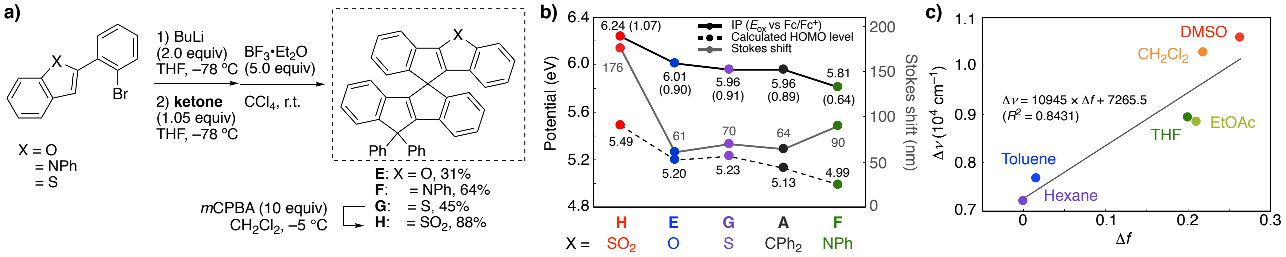

Figure 4. a) Synthesis and b) energy levels of heterocyclic spiro-CPVs.. c) Lippert-Mataga plot for compound **H**.

6. Synthesis and Materials Properties of Spiro-CPV-based Hole Transporting Materials

For the efficient performance in organic semiconducting device, hole-transporting materials (HTMs) require the stability and amorphousness of film as well as high hole mobility (μ_h). As has been already recognized for a popularly used HTM, spiro-OMeTAD, that possesses two π-systems connected by a spiro carbon atom, spiro compounds have advantages over flat π-systems on the formation of amorphous film and isotropic charge transfer. Considering small reorganization and high stability, in this work, I envisioned these requirements for HTM would be fulfilled in the spiro-CPV system. Diarylamino substituents were selected because of structural isotropy and energy level control. Spiro-CPV based HTMs showed high thermal stability in an amorphous state. Thier high glass transition temperatures (T_g = 134–176 °C), which is much higher than T_g of spiro-OMeTAD (120 °C), are expected to be advantageous for achieving device stability using these materials. Investigation of the oxidation of these compounds revealed that their radical cations have strong inter-subunit electronic interaction via spiroconjugation. It results in μ_h enhancement, while non-doped ones even exhibit higher μ_h than spiro-OMeTAD.

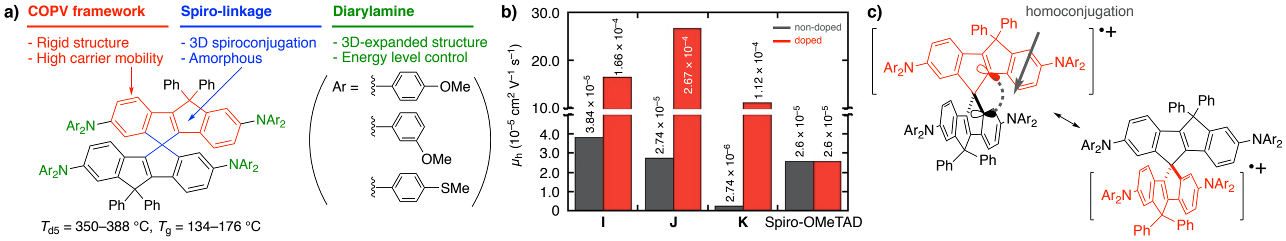

Figure 5. Spiro-CPVs based HTM a) Molecular structure. b) Hole mobilities of spin-coated film measured by SCLC methods. c) Charge delocalization through spiroconjugation in radical cation state.

7. Conclusion

During my doctoral course study, I focused on connection of flat conjugated systems via an olefinic linkage or a spiro-carbon linkage, and found that the spiro-compounds show materials properties that are more than just a summation of two conjugated systems, as revealed by the following investigations: (1) A combination of ACQ and AIE in one molecule to achieve three-stage on-off-on fluorescence switching. (2) Development of an axially chiral spiro-CPV backbone exhibiting CPL with high Φ_{FL} and high stability due to rigid hydrocarbon moiety. (3) Enhancement of k_r and Φ_{FL} by π-elongation. (4) Modification of electronic structure by the incorporation of heterocycles to achieve solvatochromism with small structural reorganization. (5) Application for HTM with high phase stability and enhanced μ_h in radical cation via spiroconjugation. Further synthetic modification based on this study will open up broader applications of organic π-conjugated materials.