論文の内容の要旨

論文題目：**Synthesis and Control of Molecular Orientations of Fused Aromatic and Heteroaromatic Compounds Possessing Flat and Twisted Frameworks**
（平面ならびにねじれた構造を有する縮合多環芳香族化合物の合成と分子配向の制御）

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Introduction

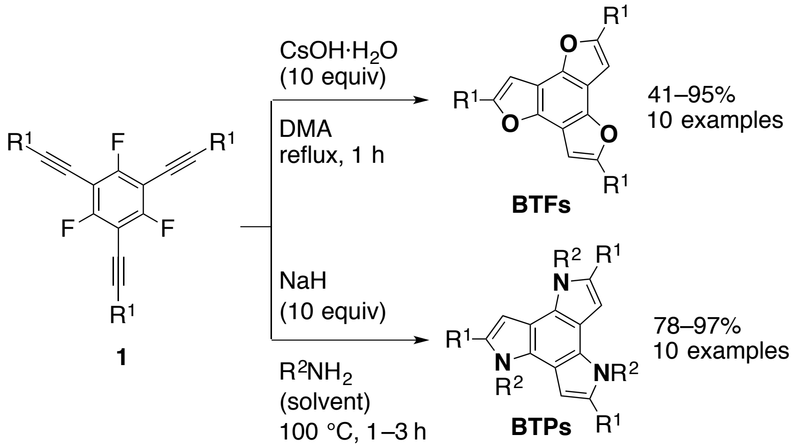
Fused aromatic and heteroaromatic compounds are important classes of compounds in the field of material science because of characteristic optical and electronic properties due to expanded π-conjugated systems. Since they are often used in the solid state, control of molecular orientations is an important factor to emerge their functions, which still remains as a challenging subject. Tuning of intermoleclular interactions is one of possible approaches to solve this problem. The author envisioned that π-conjugated systems possessing desired sizes and shapes of core structures and diverse substituents on targeted positions would enable the tuning of intermolecular interaction because they can utilize the interactions derived from both core and peripheral structures of the molecules. In his doctorial course study, the author developed novel and versatile synthetic methods for functionalized fused aromatic and heteroaromatic compounds, and confirmed that these methods work as dominant tools for the control molecular orientations with an appropriate molecular design.

Benzotrifurans (BTFs) and Benzotripyrroles (BTPs) – Compounds Possessing Flat Cores

The author developed concise synthetic methods for benzotrifurans (BTFs) and benzotripyrroles (BTPs), C_3-symmetric fused aromatic compounds possessing flat cores consisted of one benzene ring fused by three heteroaromatic rings. Reaction from a variety of 1,3,5-trialkynyl-2,4,6-trifluorobenzenes **1** with 10 equivalent of cesium hydroxide monohydrate in refluxing *N*,*N*-dimethylacetamide (DMA) gave a series of

2,5,8-trisubstituted BTF derivatives in 41–95% yield in a one-pot manner. Similar reaction from the same starting materials **1** with sodium amides, generated from sodium hydride and primary amines at 100 °C, gave diverse 1,4,7,2,5,8-hexasubstituted BTP derivatives via a tandem triple cyclization reaction in 78–97% yield (Scheme 1).

Scheme 1. Synthesis of BTFs and BTPs



Molecular and packing structures of BTF derivatives were investigated by using single crystal X-ray diffraction. It was found that BTF core and substituents of 2,5,8-triaryl-BTF derivatives were generally nearly coplanar, and the dihedral angles between the BTF core and the aryl substituents were less than 11° (Figure 1). Interestingly, subtle difference in substituents of the BTF derivatives led to significant difference in packing structures. In single crystals, 2,5,8-triphenyl-BTF formed two-dimensional layers, where the molecules were arranged in head-to-tail manner, and these layers were densely packed with an intermolecular distance of 3.32 Å (Figure 1a). On the other hand, 2,5,8-tri(2-tolyl)-BTF showed a slipped-stack columnar structure with an intermolecular distance of 3.38 Å because the 2-methyl groups inhibited the formation of a head-to-tail structure (Figure 1b). Some BTF derivatives, such as 2,5,8-tris(4-pentylphenyl)-BTF, did not show π-π stacked packing structures at all because interactions between the substituents, rather than π-π interactions between the cores, dominated the molecular assembly. These results implied that packing structures of disc-shaped molecules become controllable by changing substituents on the core structures.

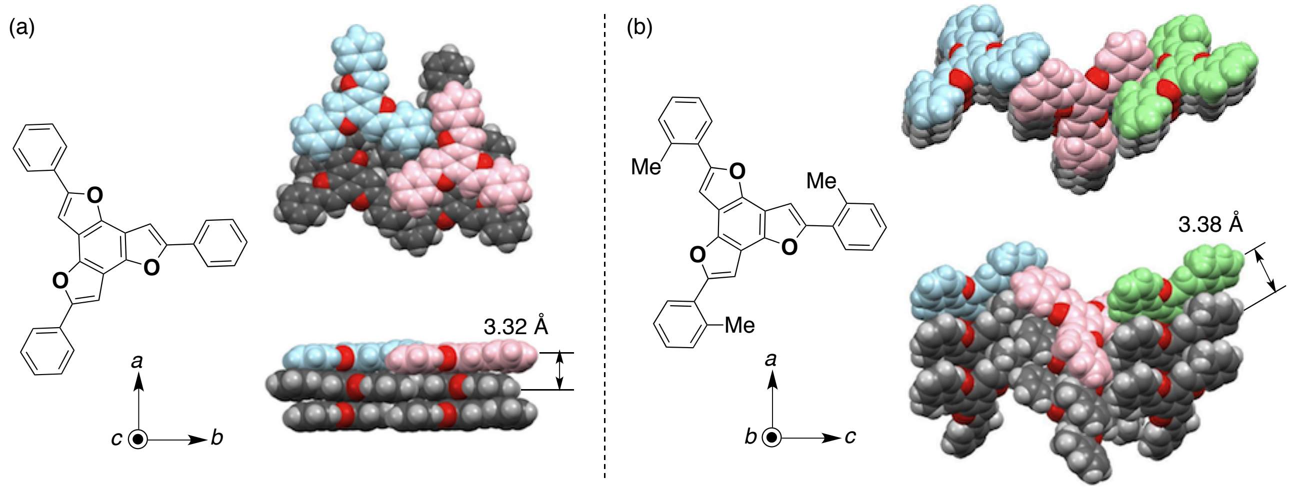
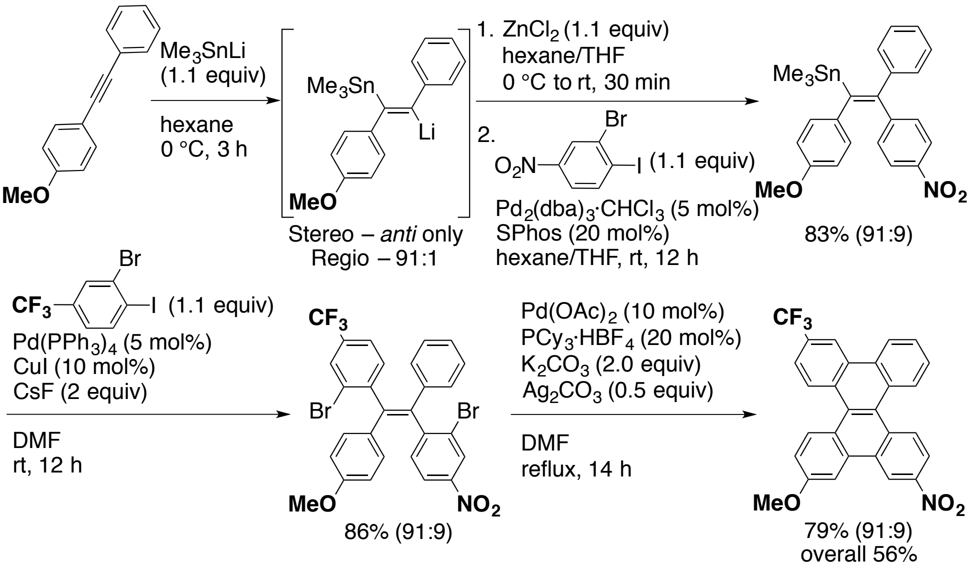


Figure 1. Versatile Packing Structures of BTF Derivatives in Single Crystals

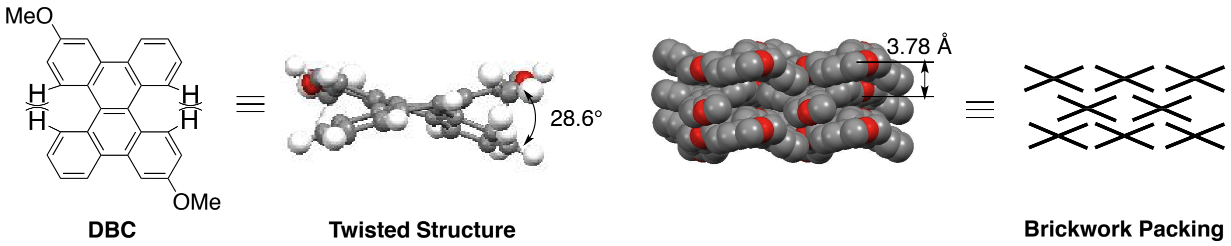
Photophysical properties of the BTF derivatives in a solution do not show any substantial differences depending on their substituents. On the other hand, photoluminescence properties of them in the solid state reflected their molecular and packing structures. The emission spectra of the well π-π stacked BTF derivatives in the solid state showed significant red-shift and broadening compared with those in the solution, while those of BTFs which do not possess π-π stacked structures did not show significant changes. This perception implied that diverse substituents on disc-shaped molecules can provide changes in properties in solid state, which will be useful for application of them for a variety of purposes.

Functionalized Dibenzo[*g*,*p*]chrysenes (DBCs) – Compounds Possessing Twisted Cores

Scheme 2. Synthesis of an Unsymmetrically Substituted Dibenzo[*g*,*p*]chrysene Derivative.



The author also established a novel synthetic method for dibenzo[*g*,*p*]crysene (DBC) derivatives, a class of polycyclic aromatic hydrocarbons (PAHs) consisting of fused six benzene rings, based on regio- and stereoselective stannyllithiation reaction of alkynes. This method enables the synthesis of a variety of functionalized DBCs, including unsymmetrically substituted one possessing both electron-donating and electron-withdrawing groups on desired positions (Scheme 2). Molecular and packing structures of DBCs were investigated by using single crystal X-ray diffraction (Figure 2). The DBC derivatives generally possess twisted molecular structures due to intramolecular steric repulsion between hydrogen atoms. Moreover, it was found that they form brickwork packing structures because of the characteristic twisted molecular structures. These packing structures are expected to be useful for the introduction of strong π-π intermolecular interaction to form multi-dimensional carrier transport paths. In fact, amorphous thin-films of DBC derivatives, which were prepared by vacuum deposition method, showed ambipolar carrier transport properties with high hole and electron mobilities. Carrier mobilities of the functionalized DBC derivatives were higher than the parent DBC compound (An example is described in Figure 2). These results indicated that the functionalization is an effective strategy to enhance their performances as materials.



$\mu_h = 4.1 \times 10^{-4}$ [cm^{2}V^{-1}s^{-1}]
$\mu_e = 1.9 \times 10^{-4}$ [cm^{2}V^{-1}s^{-1}]

(cf. Non-substituted DBC $\mu_h = 7.9 \times 10^{-5}$ [cm^{2}V^{-1}s^{-1}]
$\mu_e = 2.7 \times 10^{-5}$ [cm^{2}V^{-1}s^{-1}])

Figure 2. Molecular/Packing Structure, and Carrier Transport Properties of DBC Derivatives.

Conclusions

In his doctoral course study, the author developed the novel synthetic methods for BTFs and BTPs possessing flat cores, and DBCs possessing twisted cores. A variety of fused aromatic compounds, which have diverse substituents on the desired positions, became available by using these methods. Their properties gave a guideline for molecular design for tuning molecular orientations, and ultimately enhancing their performance as organic semiconducting materials, such as carrier mobilities.