

## 別紙 4

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## 主 論 文 の 要 旨

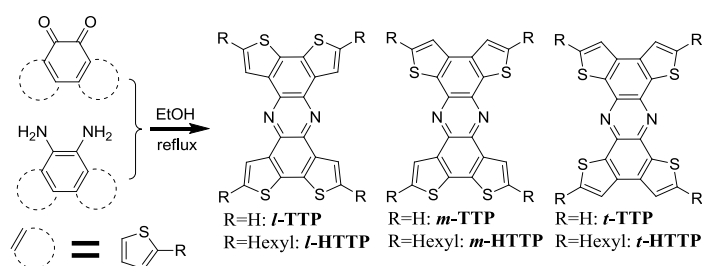
論文題目 Synthesis, Structure, and Electronic Properties of Novel Polyaromatic Hydrocarbons Annulated with Sulfur and Nitrogen Heterocycles  
 硫黄及び窒素を含むヘテロ環が縮環した新規多環芳香族化合物の  
 合成、構造、及び電子物性

氏 名 謝 永發

## 論 文 内 容 の 要 旨

In the past decades, a large number of polyaromatic materials have been developed and applied to organic electronics. Among them, polyaromatic hydrocarbons annulated with sulfur and nitrogen heterocycles have attracted significant attention mainly due to the following two reasons. Firstly, the hetero-atoms could lead to characteristic electronic structures based on their electron negativity and valency. Secondly, the intrinsic intermolecular interactions, such as S...S, and S...N contacts, affect the packing motif in the crystal, which plays a significant role in charge transport in solid state. In this thesis, two series of polyaromatic hydrocarbons annulated with heterocycles were developed for organic electronics: a series of thiophene-fused phenazines (Scheme 1), and a series of thiadiazole-fused aromatics (Scheme 2). The thiophene-fused phenazines were designed for p-channel organic transistors due to their donor ability, planar structures, and intermolecular S...S contacts. The thiadiazole-fused aromatics were designed for n-channel semiconducting materials, and for affording anion radical salts due to the acceptor ability of the thiadiazole moiety.

All of the thiophene-fused phenazines (***l*-TTP**, ***t*-TTP**, ***m*-TTP**, and their alkyl-substituted derivatives) were prepared through the formation of the phenazine skeleton by a key condensation reaction between diketones and diamines, without the need for expensive organometallic catalysts. Both symmetric and asymmetric



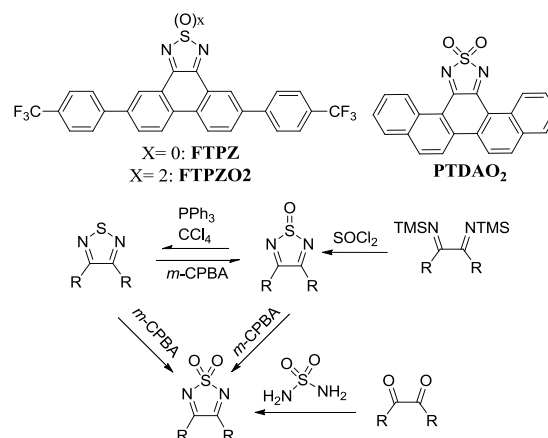
Scheme 1. Synthesis of thiophene-fused phenazines.

molecules were obtained by this method. In these derivatives, the redox potentials, and the UV-Vis absorption spectra were significantly affected by the positions of the sulfur atoms and the alkyl groups. The redox potentials of the phenazines (1.06 V, 0.83 V and 1.21 V vs.  $\text{Fc}/\text{Fc}^+$  for ***l*-HTTP**, ***m*-HTTP** and ***t*-HTTP**, respectively) were higher than that of the corresponding anthracene analogues previously reported (0.91 V and 0.95 V for ***l*-HTTA** and ***t*-HTTA**, respectively). The UV-vis absorption spectra of these compounds showed two strong absorption bands around 310 nm and between 400 nm and 490 nm, while the corresponding anthracene derivatives showed only one absorption band around 300 nm. The differences compared to the anthracene analogues in the electrochemical and optical properties were well explained by energy shifts of frontier orbitals caused by the introduction the nitrogen atoms.

From the six newly prepared thiophene-fused phenazines, four derivatives (***t*-TTP**, ***m*-TTP**, ***l*-TTP** and ***l*-HTTP**) afforded crystals from solution or by sublimation. All of these obtained crystals have  $\pi$ - $\pi$  stacking structures with  $\pi$ - $\pi$  distances in the range of 3.40 ~ 3.48 Å. Thin films of these materials were also prepared by vapor deposition and showed high crystallinity by X-ray diffraction. The transistor devices of these thin films for the alkyl-substituted derivatives exhibited reasonable p-type charge transport characteristics with hole mobilities of  $\sim 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

The thiadiazole-fused aromatics were developed by fusing the thiadiazole ring onto aromatic skeletons by various methods (Scheme 2). An advantage of thiadiazole for an electronic material is that the acceptor abilities could be tuned by changing the oxidation number at the sulfur atom on the thiadiazole ring. For example, thiadiazole-dioxide fused picene (**PTDAO<sub>2</sub>**) exhibited strong acceptor ability ( $E_{1/2} = -0.69$  and  $-1.30$  V vs  $\text{Fc}/\text{Fc}^+$ ), and thin films of **PTDAO<sub>2</sub>** showed n-type semiconducting characteristics with an electron mobility of  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . **PTDAO<sub>2</sub>** also afforded a stable anion radical salt,  $[\text{TEA}][\text{PTDAO}_2]$  with the tetraethylammonium (TEA) cation, and the magnetic property of this crystalline material was investigated by electron paramagnetic resonance ( $g = 2.0093$ ) and magnetic susceptibility ( $C = 0.54$ ,  $2J/k_B = -103$  K, and  $\theta = -5$  K).

In conclusion, the obtained  $\pi$ -conjugated aromatics with both sulfur and nitrogen hetero-atoms showed various interesting electronic properties, suggesting their potential application in organic electronics.



**Scheme 2.** Synthesis of thiadiazole-fused aromatics.