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研究課題名(和文) Novel Crystal Engineering Strategies for High Performance Semiconducting Thienoacenes

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研究成果の概要(和文)：チエノアセン類の 位にアルキルチオ基を効率的に導入する手法を確立し、これにより一連の有機半導体材料の合成に成功した。これらの化合物の結晶構造を単結晶X線構造解析により明らかにし、 位へのアルキルチオ基の導入が選択的にルブレン様の結晶構造を与えることを見出し、さらにこの特異な結晶構造が分子間のフロンティア軌道の相互作用を大きくすることを見出した。これらの化合物の単結晶及び薄膜トランジスタを作製し、ルブレンに匹敵する高い特性を示すものがあることも分かった。この研究により、本分子修飾が高性能有機半導体を開発するうえで、極めて有効な分子設計の指針であることを明らかにすることが出来た。

研究成果の学術的意義や社会的意義

The research project is the first systematic study of crystal engineering of thienoacenes by alkylthiation to develop high performance organic semiconductors for OFETs, which opens a new door to rationally design materials applied in organic electronics by control of intermolecular interactions.

研究成果の概要(英文)：In this research project firstly efficient chemistry was established to straightforwardly introduce alkylthio groups at the -position of various thienoacenes, through which the targeted thienoacene-based organic semiconductors were successfully developed. The packing structures of the as-synthesized materials were studied by single-crystal XRD analysis. The study revealed that by attaching certain alkylthio groups at the -position of linear thienoacenes, the corresponding crystal structures could be generally and selectively altered into the rubrene-like packing structure, in which efficient frontier orbital overlap could be realized. Single-crystal and thin-film OFETs were fabricated based on the as-developed materials, and some of them showed excellent performance even rivaling rubrene. The study manifested that the packing design through -alkylthiation in thienoacenes could be a real rational material design strategy to develop high performance organic semiconductors.

研究分野：Chemistry

キーワード： -Alkylthiation Thienoacene Crystal engineering OFETs

様式 C-19、F-19-1、Z-19、CK-19 (共通)

1. 研究開始当初の背景

The packing structures of organic semiconductors in the solid state play critical roles in determining their semiconducting properties in organic field-effect transistors (OFETs). The benchmark material in OFETs, rubrene, shows a so-called “pitched” π -stacking pattern, thanks to which the frontier orbital overlap between neighboring molecules can be very efficient. As a result, rubrene exhibited highest mobilities in single-crystal OFETs.¹ However, to selectively tune the packing of other organic semiconductors into the “pitched” π -stacking is extremely challenging.

In the preliminary study, methylthiation at the different positions (α and β) of benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) was conducted. Interestingly, the β -methylthiated BDT showed rubrene-like “pitched” π -stacking pattern with efficient frontier orbital overlap. These results indicated that alkylthiation on thienoacenes could be a promising strategy to develop high performance organic semiconductors rivaling rubrene in OFETs.

2. 研究の目的

Specific Aim (1): The research project firstly aimed to develop efficient chemistry to straightforwardly introduce alkylthio groups at the β -position of thienoacenes. The chemistry was proposed to be developed by utilizing novel halogenoid electrophilic reagents for the electrophilic cyclization in the synthesis of thienoacenes.

Specific Aim (2): Different alkylthio groups, i.e., alkylthio-rings were proposed to be examined in BDT to explore the substituents variation of β -alkylthiation in crystal engineering. The single crystal structures and semiconducting properties of the as-synthesized materials should be illustrated and evaluated.

Specific Aim (3): Once the β -alkylthiation strategy was established in BDT, it was proposed to be expanded to other thienoacenes with larger π -extension, such as naphthodithiophenes (NDTs) and anthradithiophenes (ADTs). The universality of this strategy in larger thienoacenes would be confirmed. Their crystal structures and semiconducting properties should be studied accordingly.

3. 研究の方法

(1) To the **Specific Aim (1)**, the electrophilic addition reaction between alkyne and halogen substance has been well known, and recently this reaction has been optimized to synthesize BDT derivatives with positively charged halogen substituents attached at the β -position of thiophene units.² Thus, the key to develop the efficient chemistry to introduce β -alkylthio groups on thienoacenes was to find novel halogenoid reagents with positively charged S atoms.

(2) To the **Specific Aim (2) and (3)**, the crystal structures of the as-synthesized materials in the solid state could be analyzed by single-crystal X-ray diffraction (XRD). The efficiency of the frontier orbital overlap of the materials in single crystals could be extracted by theoretical calculations. The semiconducting properties of the materials could be studied in single-crystal and thin-film OFETs, in which single-crystal OFETs should be more promising techniques to reveal the intrinsic charge transporting properties of the materials.

4. 研究成果

(1) Efficient chemistry was established to modify thienoacenes at the β -position with various alkylthio groups. The first halogenoid reagent coming into my mind was S_2Cl_2 , in which S atom has relatively weaker electron

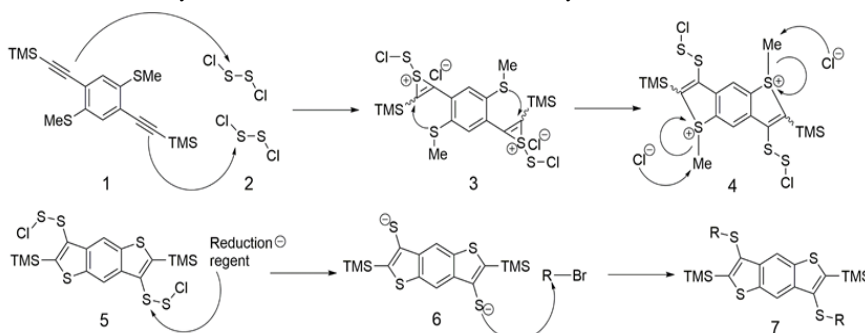


Fig.1 Working mechanism of S_2Cl_2 .

negativity than chloride. The working mechanism of S_2Cl_2 was proposed in Fig. 1. The chemistry could be done with one-pot reactions, through which various alkylthio groups could be introduced in moderate yield. Specifically, to introduce β -methylthio group, S_2Cl_2 could be replaced by MeSCl. In this case the oligomer byproducts was effectively avoided, thus the yield of reactions was improved.

(2) Continued with the preliminary results, BDT was chosen as a model system, and methylthio group was attached at the α - and β -positions, respectively. Single-crystal XRD analysis indicated that α -methylthionated BDT (α -MT-BDT) afforded the herringbone packing, whereas β -methylthionated BDT (β -MT-BDT) generated the rubrene-like “pitched” π -stacking. Furthermore, theoretical calculation suggested that the intermolecular transfer integral of HOMOs in the β -MT-BDT structure is doubly larger than that of α -MT-BDT. More interestingly, their molecular orientation on the substrate was also selectively tuned in “end-on” (α -MT-BDT) or “edge-on” (β -MT-BDT). This structural alteration gave significant effect on the transport property evaluated by the single-crystal OFETs. The β -MT-BDT-based devices showed

higher charge carrier mobility than that of α -MT-BDT-based one by one order of magnitude, which was consistent with the results on the orbital overlap and molecular orientation. In this model study methylthionation showed possibilities as a simple and powerful strategy to tune packing and semiconducting properties of materials.

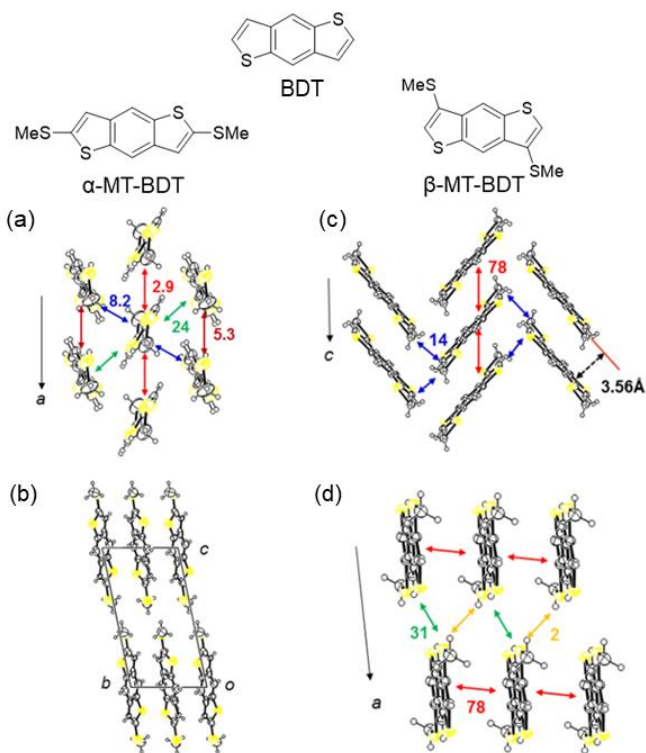


Fig. 2 Molecular and packing structures of the MT-BDTs.

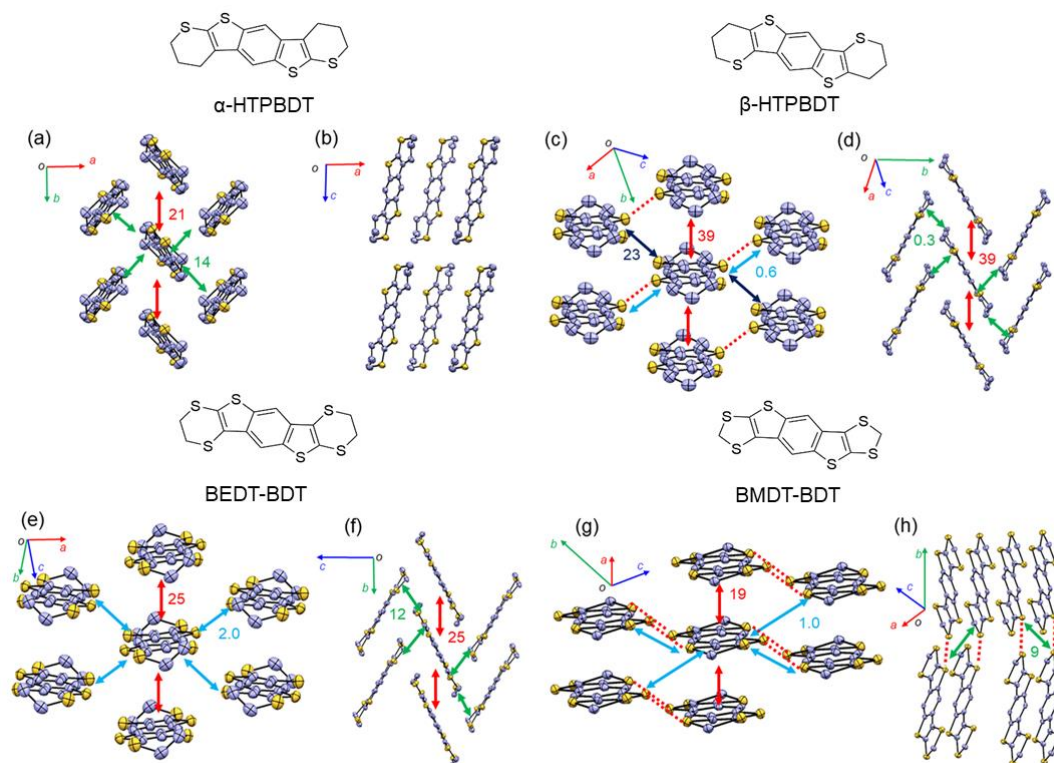


Fig. 3 Molecular and packing structures of the thiacycles modified BDTs.

(3) Next, a systematic study in the functionalization of BDT with fused-thiacycles to selectively tune the packing, molecular orientation and semiconducting properties was conducted. Six- or five-membered thiacycles were utilized to modify BDT, in such a manner that the S atoms in the thiacycles were placed at the α -, β - or both α - and β -positions of thiophene moieties in BDT. In case of the six-membered thiacycle-modified BDT derivatives, the position of S atoms turned out to be crucial to define the packing as well as molecular orientation; the derivatives with the β -S atom showed rubrene-like “pitched” π -stacking and edge-on molecular orientation on the substrate, whereas the derivative with S atoms only at the α -position adopted herringbone stacking and end-on orientation. As a result, the thin-film OFETs based on the former gave higher mobilities than the latter. On the other hand, the five-membered thiacycle-modified BDT with the smaller ring size generated totally different packing from the “pitched” π -stacking and end-on orientation, leading to low mobility in thin film OFETs.

These results clearly correlated the molecular packing, orientation and semiconducting properties with the position of the S atoms and the size of thiacycles. Our research indicated the generality of S-containing groups as a key initiator of selective tuning of the packing and molecular orientation of thienoacenes; especially S-functionalization at the β -position could achieve the rubrene-like “pitched” π -stacking, edge-on molecular orientation, and thus higher mobility in OFETs. This study not only proposed novel molecular modification strategies for thienoacenes to develop high performance semiconducting materials, but also provided a deeper understanding of how to selectively control the solid-state structures of thienoacene-based organic semiconductors.

(4) Inspired by the model study of alkylthiation on BDT in the packing control, we proposed continued study about the β -methylthiation of a series of acenedithiophenes with various π -extension for crystal engineering. The single-crystal structures of the β -MT-acenedithiophenes all showed rubrene-like pitched π -stacking. The effect of the β -methylthiation on the packing structure was analyzed by Hirshfeld surface analysis together with theoretical calculations based on the symmetry-adapted perturbation theory (SAPT), and the results clearly demonstrated that the β -methylthiation of acenedithiophenes can generally alter the intermolecular interactions through a “disrupt and induce” manner, universally realize the rubrene-like pitched π -stacking in the β -methylthionated acenedithiophenes. Although the intermolecular electronic coupling between the HOMOs of the β -MT-acenedithiophenes

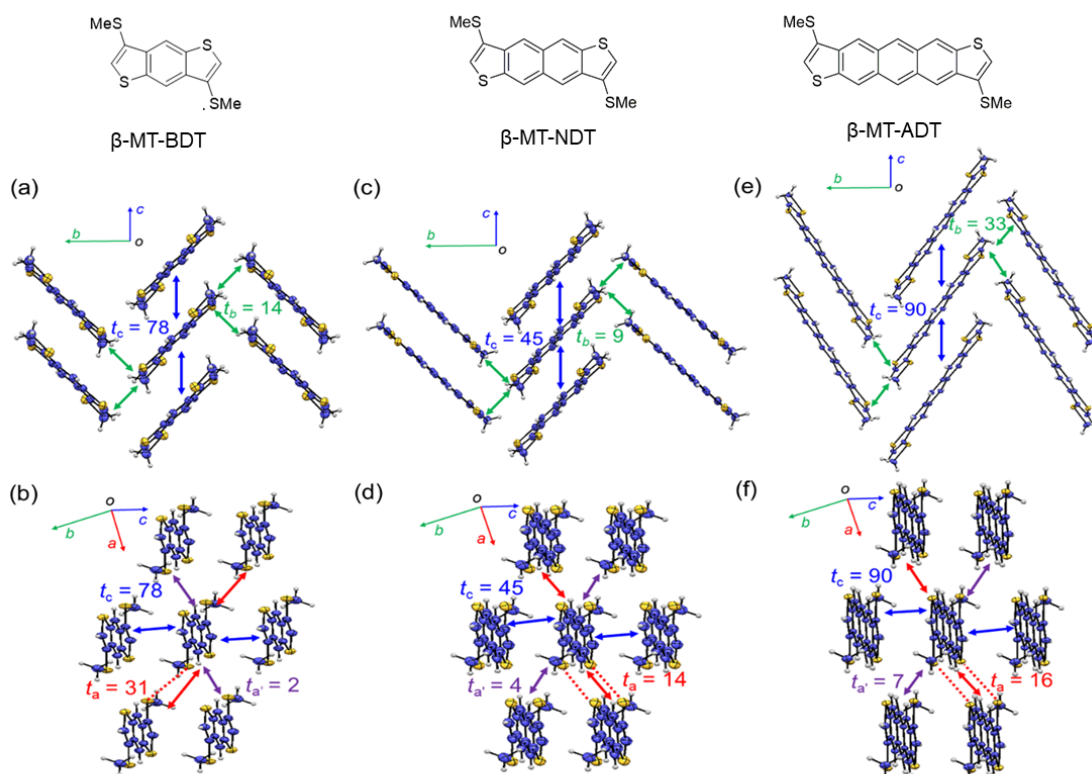


Fig. 4 Molecular and packing structures of the β -MT-thienoacenes.

in the solid state could not be straightforwardly increased by extending the molecular π -backbone, β -MT-ADT with a significantly large π -backbone realized large electronic couplings with small anisotropic electronic nature, which yield high mobility comparable to that of rubrene, up to $4.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, in SC-OFETs. From the analyses of this series of materials, we suggested a rational design strategy to realize rubrene-like high-performance organic semiconductors, which could open the door to the creation of promising materials by controlling the solid-state packing of organic semiconductors.

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6. 研究組織

- (1) 研究分担者 なし
- (2) 研究協力者 なし