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研究課題名（和文）Development of a Simple, Scalable, and Vacuum-Free Method to Fabricate Organic Semiconductor Single Crystals with Area Selectivity for High Performance Organic Field-Effect Transistor Applications

研究課題名（英文）Development of a Simple, Scalable, and Vacuum-Free Method to Fabricate Organic Semiconductor Single Crystals with Area Selectivity for High Performance Organic Field-Effect Transistor Applications

研究代表者

Ｂｕｌｇａｒｅｖｉｃｈ　Ｋｉｒｉｌｌ（Bulgarevich, Kirill）

国立研究開発法人理化学研究所・創発物性科学研究センター・特別研究員

研究者番号：６０８８０２６８

交付決定額（研究期間全体）：（直接経費）　　1,800,000円

研究成果の概要（和文）：4つのメチルカルコゲノ基を導入したメチルチオ化ピレン（MT-ピレン）はレンガ型積層構造が実現される有望な有機半導体材料として見いだされ、30cm2/Vsの高移動度とバンド的電荷輸送が実験的に確認された。近接昇華法によるルブレンやMT-ピレンなどの単結晶成長が確立され、ルブレンの液相からの結晶成長が確認された。ルブレンでは親/疎水性表面を用いたパターン化結晶成長が実現されたが、得られた結晶は小さくて厚く、OFETアレイとしての実用化は出来なかった。そこで、パターニングの代わりに基板全面を多数の結晶で覆う「間接昇華」という新手法が開発されOFETへの応用可能性が確認された（次期22K14293）。

研究成果の学術的意義や社会的意義
30cm2/Vsを超える極めて高いキャリア移動度を示し低電圧で駆動できる有機半導体材料「MT-ピレン」はディスプレイやIDタグへの応用などフレキシブルエレクトロニクスの進展に貢献することが期待できる。また、ピレンの二量体構造からMT-ピレンのレンガ型積層構造への構造変化のような、メチルチオ基の位置選択的導入による「結晶構造制御」は他のペリ縮合多環芳香族炭化水素分子に対しても有効である可能性が高く、新たな高移動度有機半導体材料開発に繋がる。さらに、本研究で開発された単結晶成長のための新手法「間接昇華」法は大面積化が容易で安価なことから近接昇華法や物理気相輸送法などに変わる手法となる可能性がある。

研究成果の概要（英文）：Methylthiolated pyrene at 1,3,6,8-positions (MT-pyrene) was rediscovered as a promising organic semiconductor material that crystallizes into a brickwork structure due to the four methylthio groups. Very high mobility of 30 cm2 V-1 s-1 and band-like transport were experimentally measured (selected as cover picture of Advanced Materials). Single crystal (SC) growth by microspacing sublimation (MSS) method was established for rubrene, MT-pyrene and other materials. The possibility of SC growth from liquid phase was confirmed for rubrene. The patterned SC growth with the use of hydrophobic/hydrophilic patterning was achieved for rubrene, but the obtained SCs were too small and too thick for practical applications in OFET arrays. A novel method based on MSS named "indirect sublimation" was developed to cover entire substrate surface with SCs instead of patterning. The application of this method to produce OFETs based on "multi-SC" films was made into a new KAKENHI project (22K14293).

研究分野：有機トランジスタ

キーワード：有機トランジスタ　単結晶優位半導体　大気中蒸着　パターン化結晶成長　表面エネルギーパターン

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１．研究開始当初の背景

OFETs have attracted increasing research attention because of their potential application in a wide range of electronic devices. Single crystals (SC) organic semiconductors are of great scientific interest not only because they can provide insight into the intrinsic properties of the organic semiconductor materials but also because highly ordered crystalline structure is beneficial for the device performance. However, in many practical cases, flexible organic semiconductors thin films that can be formed on large areas are preferred over SCs which have to be “hand-crafted” to individual OFETs by carefully placing a separately grown organic semiconductor SC onto the electrodes of a device or vice versa. The formation of SCs is also often a complicated process requiring costly systems with vacuum environments, and/or long process time.

Recently, it was reported that high quality organic semiconductors SCs can be produced by microspacing in-air sublimation (MSS). Various OSCs including pyrene, pentacene and rubrene have been confirmed to form single crystals by this method and rubrene OFETs showed record mobility among devices with similar architecture. This method is promising because it is scalable, cheap, and versatile. Even with the development of the above promising method, the application of the SC OFETs is still limited. The fabrication process of SC OFETs still could not be automated or scaled up. Interestingly, the MSS method had another potentially useful property. Rather than directly forming a solid crystal on the target substrate, which is common for physical vapor transport method, vapor that reached the substrate was reported to first form a liquid-like melt. The main idea of the proposed research was to exploit this property to produce OSC single crystals with area selectivity. The area selectivity could be achieved by preventing “droplet” formation on certain areas through suitable lyophobic/lyophilic patterning.

２．研究の目的

The purpose of the proposed research was to develop a simple and versatile method that can produce OSC single crystals suitable for application to high performance OFET arrays. More specifically, the focus was made on the crystal growth from the liquid phase achieved with MSS method in combination with hydrophobic/hydrophilic patterning to achieve patterned SC growth. Enabling the usage of organic semiconductor SCs in the OFET arrays could aid the implementation of the OFETs to the society because the device characteristics are generally improved for SCs compared to conventionally used thin films.

３．研究の方法

The research methods could be divided into three parts: establishment of patterned SC growth by MSS method in combination with hydrophobic/hydrophilic patterning; development of the novel high-performance organic semiconductor materials suitable for MSS method using “manipulation” of crystal structure strategy; application of organic semiconductor SCs to OFET arrays.

(1) Microspacing vacuum-free sublimation and patterned sublimation.

MSS method is a simple and powerful technique to grow SCs of organic materials without expensive equipment (Fig. 1). The source substrate with powder sample is placed on a heater and the target substrate is placed directly above it at a fixed distance (with help of glass or metal spacers). Although this method is often performed in air (microspacing in-air sublimation), inert atmosphere environment can be adopted for less air stable materials. The spacing can be varied in range of ~100 μm to a few mm to adjust the temperature difference between source and target substrates.

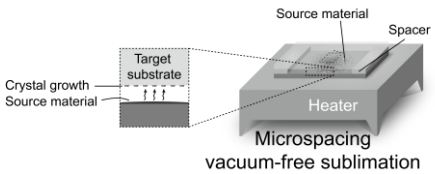

Figure 1. Microspacing vacuum-free sublimation method.

Figure 2 shows results of MSS of pentacene, rubrene, 2,9-diphenyl-DNTT (DPh-DNTT), and 2,9-didecyl-DNTT (C10-DNTT). Although thin plate-like crystals suitable for lamination and OFET fabrication were obtained for the first these materials, the crystal growth from liquid phase essential for surface energy patterning was observed only for rubrene. Even for rubrene, many crystals grew not from liquid phase but directly as free-standing plates. This was probably caused by too rapid nucleation which could be related to some powder of source material directly reaching the target substrate in addition to impurities and roughness of the substrate. The former problem was solved by in introducing a fine metal mesh between source and target substrates. In combination with rigorous cleaning of the target substrate and purification of the source material by sublimation, the nucleation of rubrene was largely suppressed and almost only liquid droplets of rubrene could be observed during MSS. Still the presence of liquid-like melt was observed only for a brief time before spontaneous crystallization occurred. Unfortunately, such effect could not be observed for most other materials despite the effort. One notable exception was C10-DNTT which formed a continuous liquid-like film, but the crystallization did not occur for this material even upon returning to

room temperature (Fig. 2d).

Next, the surface hydrophobization and patterning was performed. Octadecyltrichlorosilane (ODST) self-assembled monolayers (SAMs) were selected as hydrophobic coatings. The ODTS SAM formation was performed by vapor treatment at 120 °C in nitrogen purged glove bag followed by sonication in toluene and annealing at 150 °C in air. The ODTS-treated subface showed water contact angles of 108~110°. The hydrophobic/hydrophilic patterning was performed by exposing ODTS-treated films to vacuum ultraviolet light through a photomask followed by sonication in IPA. The exposed surface was successfully hydrophilized and demonstrated low water contact angle of < 10 °.

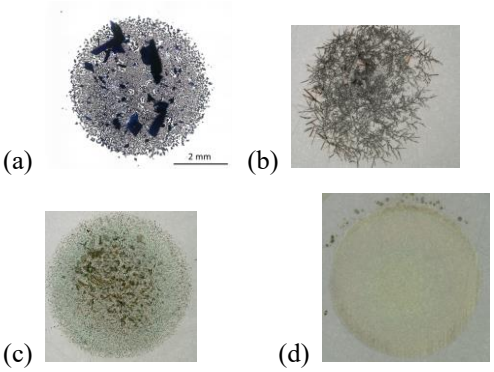

Figure 2. Result of microspacing vacuum-free sublimation for (a) pentacene, (b) rubrene, (c) DPh-DNTT, and (d) C10-DNTT.

Figure 3 shows the result of MSS of rubrene when patterned ODTS/bare patterned glass plate was used as a target substrate. Preferential growth of rubrene SCs on hydrophilic areas is clearly visible. The patterned crystal growth occurred as follows: at first, droplets form on both hydrophobic and hydrophilic areas but the ones on hydrophilic areas grow to larger size. When the temperature of the target substrate approaches the sublimation temperature of rubrene, the droplets start to evaporate. However, the crystals that already started to form in hydrophilic areas still continue to grow slightly due to supply of rubrene vapor from the even hotter source substrate (Fig. 3c). Finally, the droplets are almost completely evaporated and only the crystals of rubrene remain on the substrate. Thus, the patterned SC growth of rubrene is semi-successful: the patterning itself is achieved, but the crystals that grow on the hydrophilic area are relatively small and do not cover the hydrophilic area completely. Also, formation of some free-standing SCs could not be avoided entirely.

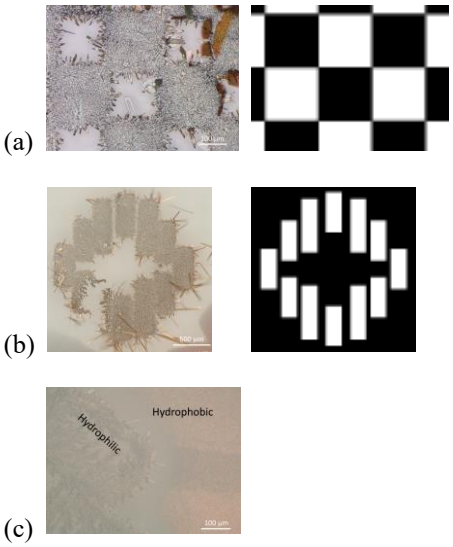

Figure 3. (a, b) The results of patterned sublimation of rubrene (left) and the photomask used to produce the hydrophobic/hydrophilic (black/white) pattern (right). (c) snapshot during (b).

The patterned SC growth was also attempted for C10-DNTT. Interestingly, the ODTS-treated surface acted as a lyophilic surface for C10-DNTT probably because this material also has alkyl chains. Thus, the droplets preferentially formed on the hydrophobic ODTS-treated surface while avoiding the hydrophilic bare surface Although the SCs did not form in the film, the patterning was also first thought to be semi-successful for C10-DNTT. However, the thinner barely visible film of C10-DNTT was confirmed to exist on the hydrophilic surface as well as on the hydrophobic surface meaning the patterning was incomplete.

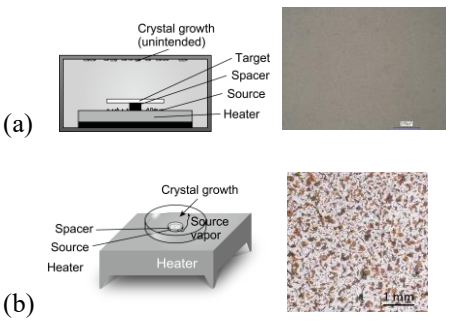

Figure 4. (a) The unexpected crystal growth during microspacing vacuum-free sublimation of MT-pyrene. (b) Improved setup for “indirect sublimation” (left) and the resulting crystals of MT-pyrene (right).

Unfortunately, the SC growth from liquid phase was not observed for MT-pyrene, a promising organic semiconductor material found by our group (see part 2 below). An interesting unrelated phenomenon was observed during MSS of MT-pyrene performed inside of the heater stage. The SC grew not only on the target substrate but also on the inside of the top glass window of the heating stage (Fig 4a, right). This was probably because the vapor of MT-pyrene that escaped from the gap between the source and the target substrates filled the inside of the heating stage and the temperature of the top inside part was suitable for the SC growth. This effect was then developed into a new method of SC growth named “indirect sublimation” by replacing the semi-hermetical heater stage with a simple petri dish and attaching the target substrate to the top inside of the petri dish. Uniformity and coverage area is largely improved (Fig. 4b) for indirect sublimation compared to MSS because the direct passes between the source and target substrates are blocked and the SC growth is now independent of initial source material distribution. At first glance, this new method is

hardly related to the purpose of this project. Its potential usefulness for fabrication of OFET arrays will be discussed in part 3.

(2) Development of novel high-performance organic semiconductor materials.

Crystal structure plays a major role in determining the charge transport properties of organic semiconductors along with their molecular properties. One of the most common structures of the molecular semiconductors is herringbone and it is observed for many acenes, and heteroacenes such as pentacene and DNTT. Herringbone structure realizes two-dimensional (2D) electronic structure and carrier mobilities of > 1 $cm^2 V^{-1} s^{-1}$ were demonstrated for pentacene and DNTT based OFETs. The other promising crystal structures for molecular organic semiconductors are pitched π-stack and brickwork structures which offer highly efficient orbital overlap along the π-stacking direction(s). However, molecular semiconductors that crystallize into these structures have remained a minority. The examples are rubrene (pitched π-stack) and bis((triisopropylsilyl)ethynyl)pentacene (TIPS-pentacene, brickwork).

It was recently reported by our group that the crystal structure can be rationally controlled by methylthiolation. The crystal structure of benzo[1,2-b:4,5-b′]dithiophene (BDT) (herringbone) could be changed to pitched π-stack and brickwork by methylthiolation (βMT-BDT) and methylselenolation (βMS-BDT), respectively at the β-positions. A systematic study on βMT-BDT related compounds was performed to understand the effects of chalcogen atom on molecular and crystal structures. A 3 x 3 matrix of the compounds with oxygen, sulfur, and selenium in the core (BDF, BDT, and BDS, respectively) and in the methylchalcogeno groups at β-positions (βMO, βMT, and βMS, respectively) was evaluated. It was found not only that the methylchalcogenolation is a powerful tool to modify the crystal structure, but also that each methylchalcogeno group has its own features that largely influence the intermolecular interactions and electronic structures in the solid state. These results are under revision at Chinese Journal of Chemistry.

Following this strategy, methylthiolation of pyrene was performed. Unsubstituted pyrene crystallizes into a dimeric herringbone structure which offers basically no charge transport at large distance. Tetramethylthiolation at 1,3,6,8-positions (MT-pyrene) resulted in structural change into the brickwork structure. MT-pyrene itself was first synthesized nearly 30 years ago for the use in charge transfer complexes, but its crystal structure and OFET characteristics were not elucidated then.

OFETs of MT-pyrene were fabricated and evaluated using SCs grown by MSS and PVT methods. The OFETs demonstrated almost ideal characteristics without hysteresis and showed very high mobility of ~30 $cm^2 V^{-1} s^{-1}$ (Fig. 5, left) at low voltage operation of 5 V. The carrier mobility was much higher than predicted using the hopping model (~4 $cm^2 V^{-1} s^{-1}$) which was explained by measuring the temperature dependence of mobility and experimentally confirming the band-like transport in MT-pyrene. Also, the band calculations suggested the large HOMO band widths and small effective masses which was another evidence supporting band-like transport. These results were published in Advanced Materials and were selected as a cover picture (Fig. 5, right).

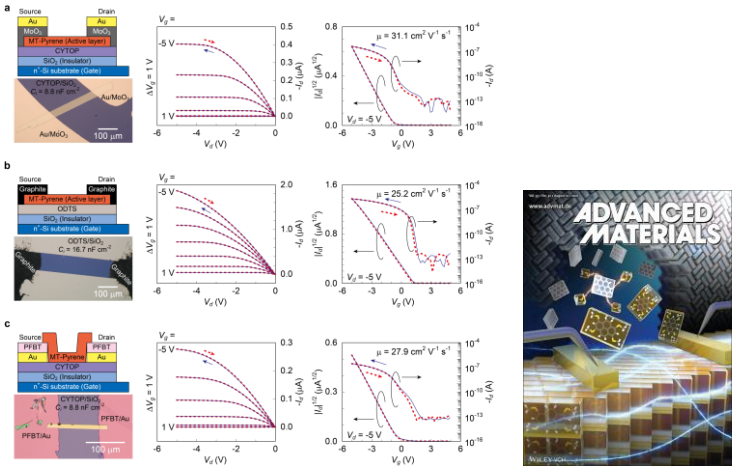

Figure 5. OFET characteristics of MT-pyrene for various device architectures.

A systematic study on MT-pyrene-related compounds was performed with methoxy and methylseleno groups at 1,3,6,8-positions of pyrene (MO- and MS-pyrene, respectively). The crystal structure and transport properties were evaluated, and it was found that MO- and MS-pyrene also crystallize into similar brickwork structures. On the other hand, the transport properties largely differed and the mobilities were only 0.03 and 7.3 $cm^2 V^{-1} s^{-1}$ for MO- and MS-pyrene, respectively. The differences with MT-pyrene were understood to mainly be the poor electronic structure of MO-pyrene and unfavorable (close to one-dimensional) crystal structure of MS-pyrene. The results are under revision in Chemistry of Materials.

A study on DNTT derivatives 2,9-DPh-DNTT (referred as simply DPh-DNTT in part 1) and 3,10-DPh-DNTT was conducted. It was found that although these materials afford very similar herringbone crystal structures and could hardly be distinguished by their predicted hopping and band properties, the experimentally measured charge transport properties were largely different. 2,9-DPh-DNTT demonstrated high carrier mobility of > 15 $cm^2 V^{-1} s^{-1}$ and band-like transport, while the mobility of 3,9-DPh-DNTT was moderate (~8 $cm^2 V^{-1} s^{-1}$) and the charge transport was almost temperature independent. These results were understood by showing that 3,10-DPh-DNTT is more susceptible to dynamic disorder with the help of

molecular dynamics simulations. These results were published in ACS Materials Letters.

Although MT-pyrene and DPh-DNTT are very promising materials in terms of charge transport properties, unfortunately they (and also MS-pyrene) were unsuitable for patterned sublimation as was mentioned in part 1. However, large quantity of high quality SCs of MT- and MS-pyrene could be obtained at high coverage using the newly developed indirect sublimation method. Application of such SCs to OFETs and OFET arrays will be discussed in the next part.

(3) Application of organic semiconductor single-crystals to OFET arrays.

Patterned sublimation of rubrene was performed using ODTS-treated/bare patterned SiO_2/Si wafers as target substrates. Similar results to those performed on glass target substrates (Fig. 3) were obtained. To test the OFET operation of such SCs, the colloidal graphite electrodes were painted. Unfortunately, such OFETs barely functioned which was natural considering poor coverage and interconnection of SCs (Fig. 6). The process optimization for patterned growth of rubrene was continued, but functioning SC could be obtained only individually and not as spanning or covering the whole hydrophilic area.

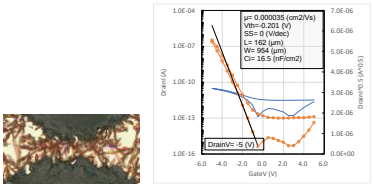

Figure 6. Rubrene OFET fabricated using SCs grown by MSS on ODTS/bare SiO_2/Si substrate.

Although unrelated to patterning, the indirect sublimation (Fig. 4b) conditions were optimized for MT-pyrene, MS-pyrene, and rubrene. Very similar SCs could be obtained at high coverage on a large surface area similar to Figure 4b, right. This method is useful even compared to PVT because it produces SCs on a scalable flat surface as opposed to inside of a tube for PVT. All the grown SCs are easily accessible meaning that material efficiency is high. Simple pressing of such substrate covered with SCs onto a CYTOP-coated SiO_2/Si substrate resulted in a so called "multi-SC" (MSC) film. OFET arrays using MT-pyrene MSC films were fabricated by depositing MoO_x/Au electrodes through a metal shadow mask (Fig. 7a). For the relatively low-coverage MSC films, the on/off characteristics were good, and the carrier mobility was as high as 20 $cm^2 V^{-1} s^{-1}$ (Fig. 7b). However, there were potential device failures especially for smaller devices due to gaps in the MSC film. The complete coverage could be achieved by multiple press transfers (3-5 times). Such films operated with high mobility comparable to SC-FETs (~28 $cm^2 V^{-1} s^{-1}$), but the on/off characteristics were degraded (Fig. 7c). The degradation on the on/off characteristics was probably caused by some SCs not being completely attached to the substrate surface (not completely applied gate voltage to some SCs). Although various press transfer conditions were tried including pressing against softer substrate, blowing / shaving off the excess crystals, and applying vacuum after transfer, the characteristics could not be improved within the research period. It was decided that a sophisticated mechanical setup is required to apply controlled and uniform force during press transfer (made into a new KAKENHI project, 22K14293).

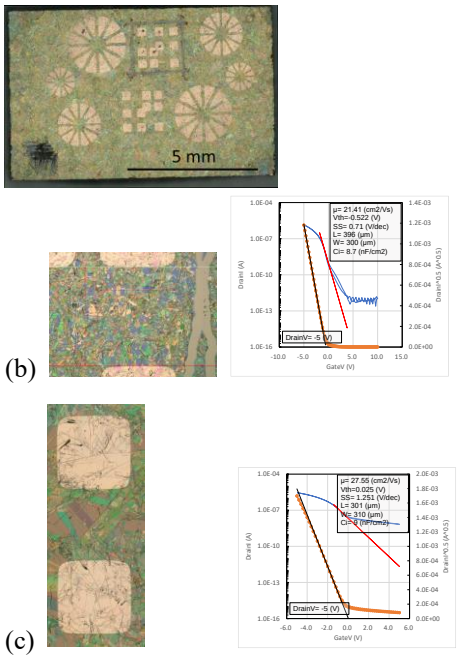

Figure 7. (a) MT-pyrene MSC film OFET array. (b, c) MT-pyrene MSC OFETs. (b) Relatively low-coverage MSC film, (c) high-coverage MSC film.

4．研究成果

Although the initial idea of this research to fabricate OFET arrays using patterned SC growth was not realized fully, it led to development of a novel promising method for organic semiconductor SC growth and application in OFET arrays. This new "indirect sublimation" method may even be superior to the method originally proposed because of its simplicity, scalability, and applicability to wide range of materials. Notable advances in development and study of materials applicable for MSS method were made. Methylchalcogenation and its effect was studied in detail for the BDT and related cores (article under revision in Chinese Journal of Chemistry). Methylthiolated pyrene at 1,3,6,8-positions (MT-pyrene) was rediscovered as a promising organic semiconductor material that crystallizes into a brickwork structure and shows very high mobility of ~30 $cm^2 V^{-1} s^{-1}$ (selected as a cover picture of Advanced Materials). Also, promising DNTT derivatives, 2,9-DPh-DNTT and 3,10-DPh-DNTT were studied and high mobility (> 15 $cm^2 V^{-1} s^{-1}$) of 2,9-DPh-DNTT SCs OFETs compared to 3,9-DPh-DNTT was rationally understood by implementing dynamic disorder simulations (published in ACS Materials Letters). Novel organic semiconductor materials, especially MT-pyrene were in good compatibility with the indirect sublimation method and the research will continue in my next KAKENHI project.

５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　1件／うちオープンアクセス　1件）

１．著者名 Takimiya Kazuo、Bulgarevich Kirill、Abbas Mamatimin、Horiuchi Shingo、Ogaki Takuya、Kawabata Kohsuke、Ablat Abduleziz	４．巻 33
２．論文標題 “Manipulation” of Crystal Structure by Methylthiolation Enabling Ultrahigh Mobility in a Pyrene‐Based Molecular Semiconductor	５．発行年 2021年
３．雑誌名 Advanced Materials	６．最初と最後の頁 2102914～2102914
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/adma.202102914	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Takimiya Kazuo、Bulgarevich Kirill、Horiuchi Shingo、Sato Aoi、Kawabata Kohsuke	４．巻 4
２．論文標題 Bandlike versus Temperature-Independent Carrier Transport in Isomeric Diphenyldinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophenes	５．発行年 2022年
３．雑誌名 ACS Materials Letters	６．最初と最後の頁 675～681
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsmaterialslett.2c00084	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計2件（うち招待講演　0件／うち国際学会　0件）

１．発表者名 Kirill Bulgarevich、瀧宮和男、Mamatimin Abbas、堀内信吾、大垣拓也、川畑公輔、Abduleziz Ablat
２．発表標題 メチル化ピレン単結晶の高性能 有機トランジスタ
３．学会等名 第82回応用物理学会秋季学術講演会
４．発表年 2021年

１．発表者名 Kirill Bulgarevich、瀧宮 和男、大垣 拓也、堀内 信吾
２．発表標題 カルコゲン原子の違いによるメチルカルコゲノ化ピレン の結晶構造と電荷輸送特性への影響
３．学会等名 第６８回応用物理学会春季学術講演会
４．発表年 2022年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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https://www.riken.jp/press/2021/20210705_4/index.html
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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関