受賞講演・特別講演 | 受賞講演・特別講演：受賞講演・特別講演

2026年3月19日(木) 15:55 ~ 17:25 | B1326（13号館 [2階] 1326）

[B1326-3vn] 受賞講演・特別講演

座長：岡本 敏宏、宮田 潔志

英語 若い世代の特別講演

15:55 ~ 16:25

[B1326-3vn-01] ヘテロ環縮合キノイド骨格を基盤とした狭バンドギャップ有機半導体の設計

○川畑 公輔[1,2] (1.東北大、2.理研)

日本語 若い世代の特別講演

16:25 ~ 16:55

[B1326-3vn-02] 材料化学的アプローチによるスズペロブスカイト太陽電池の高性能化

○中村 智也[1] (1.京大化研)

日本語 若い世代の特別講演

16:55 ~ 17:25

[B1326-3vn-03] 高性能ペロブスカイト太陽電池を志向した多脚型正孔回収単分子膜材料の開発

○チョン ミンアン[1] (1.京都大学化学研究所)

Molecular Design of Small-Bandgap Organic Semiconductors Incorporating Fused Heterocyclic Quinoids

([1]*Graduate School of Science, Tohoku University*, [2]*RIKEN, CEMS*) ○Kohsuke Kawabata[1,2]
Keywords: *Organic Semiconductor*; Small Bandgap; Quinoid; Near-infrared Absorption; Carrier Transport

Small-bandgap organic semiconductors are attractive optoelectronic materials due to their optical absorption and emission in the near-infrared (NIR) region as well as their ambipolar carrier transport properties. In particular, materials with a small bandgap of less than 1.1 eV (corresponding to a wavelength of 1100 nm) could be a promising alternative to silicon. To develop such small-bandgap organic semiconductors, a donor-acceptor (D-A) approach is effective for reducing the bandgaps; however, raising the HOMO level often compromises air stability during carrier transport. Therefore, lowering the LUMO level by incorporating highly electron-deficient acceptor units is import for the development of small-bandgap materials.

To this end, we have explored a series of fused heterocyclic quinoids having two key structural features, i) proaromatic benzo- and naphtho-quinodimethane substructures and ii) electron-withdrawing carbonyl termini, both of which can stabilize the anionic state of the skeleton thus resulting in the highly electron-deficient nature. Further structural modification of heteroatoms, conjugation length, and the shape/symmetry are also important for fine-tuning the electronic structures of the quinoidal skeletons. We systematically incorporated the quinoidal skeletons into D-A oligomers and polymers and investigated structure-property relationships of their optical and electronic properties as well as carrier transport properties for rational molecular design of small-bandgap organic semiconductors (Fig. 1).

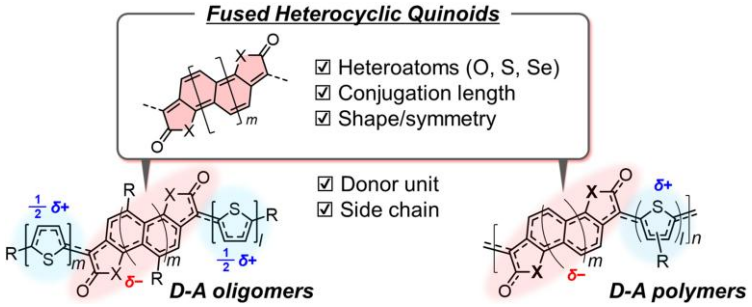


Fig. 1. Molecular design of D-A semiconducting oligomers and polymers in this work.

Our initial study focused on dithienyl D-A-D triads incorporating a series of thienoquinoids **1**–**5** (Fig. 2a). With the π-extension of the quinoidal structures from **1**, the triads **2**–**5** exhibited significantly low-lying LUMO energy levels (−4.2 to −4.3 eV) as well as absorption in the visible to NIR region. These results indicated the highly electron-deficient nature of the quinoidal skeletons, particularly the naphthodithiophenedione skeletons. Then, one of the naphthodithiophenediones was flanked with extended oligothiophene donors for

further reducing the bandgap (Fig. 2b). With the extension of the donor units, the absorption maxima of **6**–**8** in solution were increased from 690 to 834, and to 903 nm, all of which, however, were blue-shifted in thin films. In sharp contrast, **9**–**11** with the same D-A-D backbone as **6**–**8** but with solubilizing substituents at the quinoidal core instead of the flanking donor units exhibited significant red-shifts of their absorption bands from the solution to the thin-film state. Single-crystal X-ray analyses revealed that the position of the solubilizing substituents critically affects the intermolecular arrangement of the transition electric dipole moment, where the end- and core-alkylated triads form side-by-side (H-aggregation) and slip-stacked (J-aggregation) arrangements, respectively.

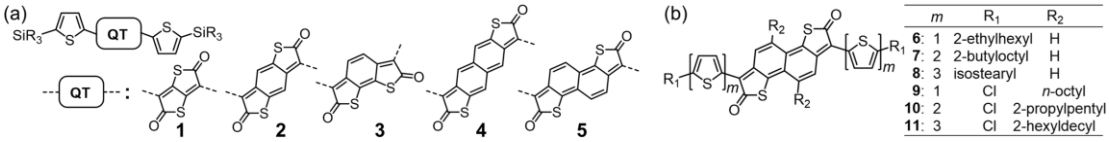


Fig. 2. Thienoquinoid-based D-A-D triads.

Another series of D-A-D triads based on the fused heterocyclic quinoids with oxygen and selenium atoms instead of sulfur atoms were also investigated (BXs and NXs in Fig. 3a). Regardless of the chalcogen atom, the quinoidal structures are highly electron-deficient. Thus, all BXs and NXs showed small bandgaps with low-lying frontier orbital energy levels, enabling air-stable hole and electron transport. Interestingly, the oxygen analogs BO and NO showed one-order-of-magnitude higher mobilities than those of the sulfur and selenium analogs. Single-crystal X-ray analyses indicate that the smaller sizes of the oxygen atom compared to the sulfur and selenium atoms leads to coplanar and rigid backbones, thus suppressing structural and energetic disorder in the solid-state structures, which results in enhanced carrier mobilities. Furthermore, by extending BXs into polymeric systems PXs (Fig. 3b), marked reduction of the optical bandgap to as low as 0.88 eV and significant improvements in the carrier mobilities of up to 2 $cm^2 V^{-1} s^{-1}$ were achieved, where the striking chalcogen-atom-dependance on the mobility was preserved.

These results highlight the great potential of acenedichalcogenophenediones as building units for small-bandgap organic semiconductors. In the presentation, detailed structure-property relationships for rational molecular design will be discussed.

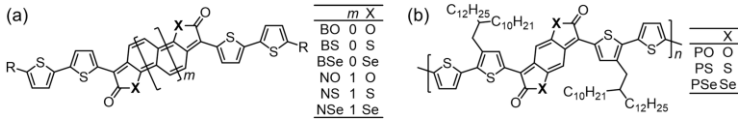


Fig. 3. Acenedichalcogenophenedione-based oligomers and polymers.

1) K. Kawabata, M. Saito, I. Osaka, K. Takimiya, *J. Am. Chem. Soc.* **2016**, *138*, 7725. 2) K. Kawabata, I. Osaka, M. Sawamoto, J. Zafra, P. Burrezo, J. Casado, K. Takimiya, *Chem. Eur. J.* **2017**, *23*, 4579. 3) K. Kawabata, K. Takimiya, *Chem. Eur. J.* 2021, 27, 15660. 4) K. Kawabata, K. Takimiya, *Chem. Mater.* **2023**, *35*, 7628.) K. Kawabata, K. Mashio, K. Takimiya, *Chem. Mater.* **2024**, *36*, 11920.

材料化学的アプローチによるスズペロブスカイト太陽電池の高性能化

（京大化研[1]）○中村 智也[1]
Materials Chemistry Approach for Efficient Tin Halide Perovskite Solar cells
([1]*Institute for Chemical Research, Kyoto University*) ○Tomoya Nakamura[1]

Tin-based perovskite semiconductors are promising lead-free materials with low environmental impact for next-generation photovoltaics. However, the power conversion efficiency of tin-based solar cells remains significantly lower than their lead-based counterparts. This presentation summarizes the key challenges limiting the performance of tin perovskite solar cells and introduces our latest research findings based on materials chemistry approaches to address these issues.
Keywords : Solar Cells; Tin Perovskite; Materials Chemistry

金属ハライドペロブスカイト（一般式 ABX_3：A = 1 価カチオン，B = Pb^{2+}, Sn^{2+}，X = I^-, Br^-, Cl^-）を用いた太陽電池は、塗布により作製できる次世代太陽電池として注目を集めている。特に、B サイトにスズ（Sn）を用いた系は環境負荷低減の観点から期待されているが、その光電変換効率は鉛（Pb）を用いたものの半分程度にとどまっている。本研究では、Sn と Pb の化学的性質の違いに基づき、性能低下の要因となるボトルネック課題を抽出し、以下の材料化学的アプローチによりその改善に取り組んだ。

1. 材料の高純度化：Sn^{4+}不純物の除去

Pb と Sn は同じ 14 族元素であるが、Pb^{2+}が安定であるのに対し、Sn^{2+}は容易に酸化され Sn^{4+}を生じる（図 a）。Sn^{4+}が混在すると、p 型ドーピングにより太陽電池特性を著しく低下させる要因となる。そこで、8π 電子系化合物であるジヒドロピラジン誘導体（TM-DHP）を合成し、前駆体溶液から Sn^{4+}種を取り除く手法を開発した。TM-DHP は溶液中で添加剤 SnF_2 と反応して Sn^0 ナノ粒子を生成し、これが溶液中の Sn^{4+}種を効果的に捕捉する「Sn^{4+}スカベンジャー」として機能することを見出した。本手法により、Sn^{4+}含有率が極めて低い（<0.1%）高純度 Sn ペロブスカイト薄膜の作製に初めて成功した[1]。本手法は、室内用途やタンデム太陽電池に適した広バンドギャップ材料にも適用可能であり、再現性よく太陽電池性能を向上させることができた[2]。

2. 界面パッシベーション法の開発

材料中の不純物に起因する欠陥に加え、薄膜形成時に生じる各イオンの空孔欠陥（vacancy）も、太陽電池特性低下の要因となる。結晶内部よりも欠陥が生じやすいペロブスカイト層表面の構造修飾法を開発した（図 b）。A サイトのパッシベーション材料として、二つのアンモニウム基をもつエチレンジアンモニウム（EDA^{2+}）と、アンモニウム基とカルボキシル基をもつグリシン（Gly）を用いた。これらの分子を上下界面に配置し、電荷回収層に向かうダイポール（双極子）を形成することで、キャリアを効率的に取り出すことが可能になった。その結果、Sn–Pb 混合型ペロブスカイト太陽電池で、Sn を含む系として世界最高値となる 23.6%の光電変換効率を達成した[3]。この手法は純 Sn ペロブスカイト太陽電池にも有効であり、光電変換効率を 9.9%から 11.4%まで向上させることができた[4]。また、B サイトのパッシベーション材料としてトリプチシル基を導入したクロロスタニレンを開発し、ペロブスカイト層表面

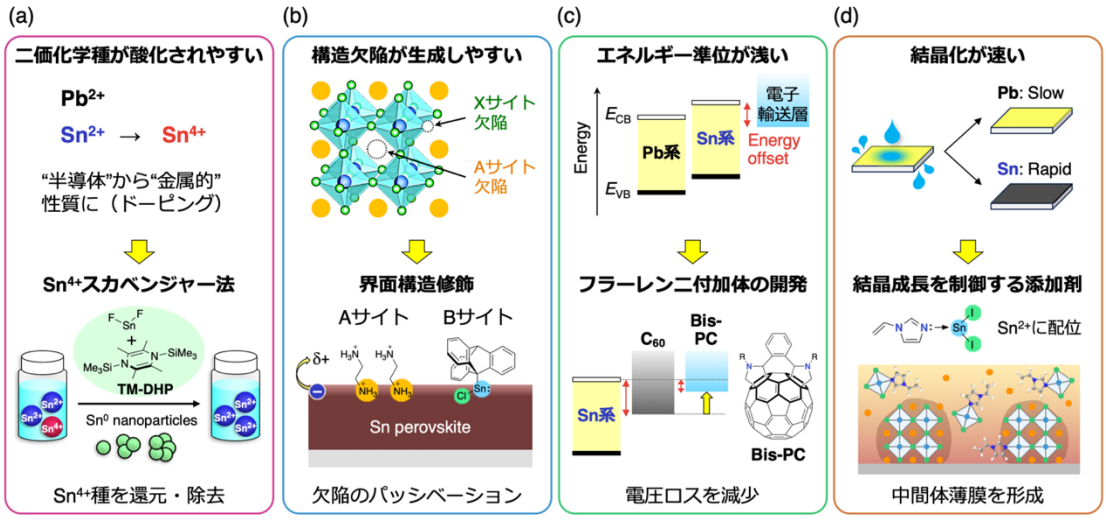
への塗布により開放電圧を向上できることを見出した[5]。

3. 電子輸送材料のエネルギー準位制御

Sn ペロブスカイトの伝導帯準位は Pb 系よりも浅く、電子回収材料 C_{60} の LUMO 準位とのエネルギー差が開放電圧ロスの要因となる（図 c）。LUMO 準位の浅いインデン-C_{60} 二付加体（ICBA）が有効とされるが、付加結合位置の組み合わせにより異性体混合物を生じる課題があった。そこで、フェニレン基で架橋した二つのピロリジン環を導入したフラーレン二付加体（Bis-PC）を開発した。異性体を含まない純粋な化合物として単離した Bis-PC を用いることで、12.3%の光電変換効率と、従来の ICBA（異性体混合物）よりも高いデバイス安定性を実現した[6]。

4. 結晶成長制御剤を用いた Sn ペロブスカイト成膜法の開発

Sn ペロブスカイトは Pb 系と比べて結晶化が速く、通常の成膜法（スピンコート中に貧溶媒を滴下して結晶化させる方法）では親水的な下地の上にしか成膜できず、作製できるセルの大きさも 1 cm^2 以下に限られていた（図 d）。そこで、Sn イオンに対し強い配位能をもつイミダゾール誘導体を「結晶成長制御剤」として用いる独自の成膜法を開発した。本手法では、減圧乾燥過程で形成される非晶質錯体中間体を経由することで結晶成長を遅延・制御できる。これにより、従来困難であった疎水性基板上への緻密な成膜や、ダイコーターを用いた大面積塗工が可能となった[7]。



1) T. Nakamura, T. Sasamori, H. Ohkita, Y. Kanemitsu, A. Wakamiya* et al., *Nat. Commun.* **2020**, *11*, 3008.
2) T. Nakamura, Y. Kanemitsu, A. Wakamiya* et al., *ACS Appl. Energy Mater.* **2022**, *5*, 14789.
3) S. Hu, T. Nakamura, K. Marumoto, K. Tajima, Y. Kanemitsu, A. Wakamiya* et al., *Energy Environ. Sci.* **2022**, *15*, 2096.
4) S. Hu, J. Pascual, K. Tajima, T. Nakamura, A. Wakamiya* et al., *ACS Appl. Mater. Interfaces* **2022**, *14*, 56290.
5) A. Hasegawa, T. Nakamura,* A. Wakamiya* et al., *Chem. Mater.* **2025**, *37*, 6246.
6) T. Nakamura,* T. Nagai, H. Yoshida, Y. Kanemitsu, A. Wakamiya* et al., *Chem. Sci.* **2025**, *16*, 2265.
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Development of Multipodal Hole-Collecting Monolayer Materials for Perovskite Solar Cells

(*Institute for Chemical Research, Kyoto University*) ○Minh Anh Truong
Keywords: Perovskite Solar Cells; Hole-Collecting Materials; Monolayer; Chemisorption

As solar energy is the most abundant renewable energy source, the development of solar cells with high efficiency, long term stability, and low cost is undoubtedly a key to realize a carbon-neutral society. Perovskite solar cells (PSCs) have been considered as one of the most promising photovoltaic technologies and attracted worldwide attention due to their high power conversion efficiencies (PCEs) and low-cost solution processing.

Besides the film and interfacial engineering of the perovskite layer, the development of hole-collecting materials (HCMs) is a critical factor in boosting the performance of PSCs, especially inverted PSCs. In this device structure, HCMs are not only responsible for hole extraction and transport but also influence the deposition of perovskite films. Compared with conventional polymeric HCMs, which usually requires thick layers (> 10 nm), anchorable molecules that can spontaneously adsorb onto the surface of transparent conducting oxide (TCO) substrates to form a monolayer are more suitable for high-performance and scalable PSCs.[1,2] This suitability arises from their low material consumption, minimal parasitic absorption, simplified fabrication processing, and facile molecular structure modification. However, to date, reported anchorable HCMs have been limited to monopodal molecules consisting of a π-conjugated core connected to a single phosphonic or carboxylic acid anchoring group (Figure 1). After adsorption onto the TCO surface, these molecules typically adopt an edge-on orientation, which is unfavorable for efficient hole extraction and transport.

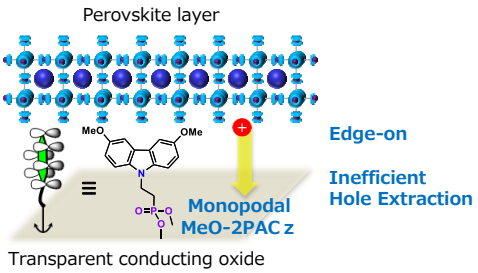

Figure 1. Conventional Monopodal Monolayer Materials.

In our group, we have proposed a multipodal anchorable HCM strategy and demonstrated its superior advantages over the monopodal counterpart. As the first generation of our multipodal hole-collecting monolayer materials, we developed a tripodal molecule composed of a triazatruxene core connected to three propyl phosphonic acid anchoring groups (**PATAT**, Figure 2).[3] We demonstrated that, after being chemically adsorbed onto the TCO surface,

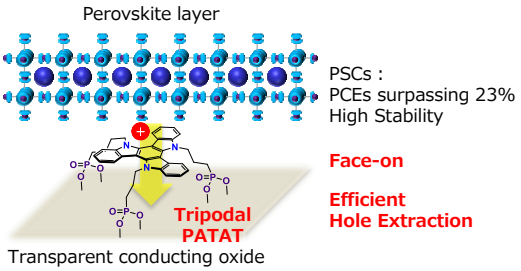

Figure 2. Tripodal **PATAT** Molecule.

PATAT molecules tend to form a face-on oriented monolayer, resulting in enhanced hole collection compared to their monopodal and edge-on oriented counterpart. Consequently, inverted PSCs using the **PATAT** monolayer as the hole-collecting layer achieved PCEs of up to 23%, along with high operational stability. However, as all phosphonic acid groups anchor to the TCO surface, the **PATAT** monolayer shows a hydrophobic surface, which may impede the spreading of the hydrophilic perovskite precursor solution and thereby constitute an obstacle to large-area application.

To address the surface wettability issue, we developed a tetrapodal molecule, **PATTI** (Figure 3), as a second generation of our multipodal HCM strategy. **PATTI** consists of a saddle-shaped indole-fused cyclooctatetraene (**COT**) core bearing four propyl phosphonic acid anchoring groups. Owing to the saddle-shaped **COT** skeleton, after chemisorbed on TCO substrates, two of the four phosphonic acid groups point upward, resulted in a hydrophilic surface and improved surface wettability.

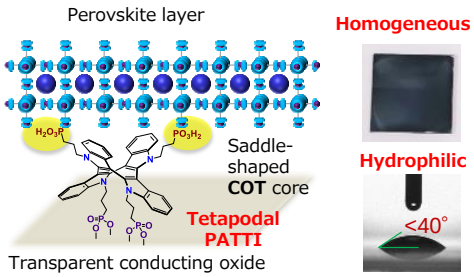

Figure 3. Tetrapodal **PATTI** Molecule.

In inverted PSC fabrication, the HCM layer is typically deposited prior to the perovskite layer, a multistep process that is undesirable for low-cost production. To reduce deposition steps, we developed a tripodal **CATAT** molecule (Figure 4). Owing to its carboxylic acid anchoring groups, **CATAT** exhibits weaker interaction with the perovskite precursor components, a larger diffusion coefficient, and higher surface energy than **PATAT**, making it more suitable for a one-step co-deposition process in which **CATAT** was directly added into the perovskite precursor solution. After spin-coating the mixed precursor solution, **CATAT** is predominantly located at the perovskite bottom surface, facilitating charge extraction and enabling high-performance PSCs.

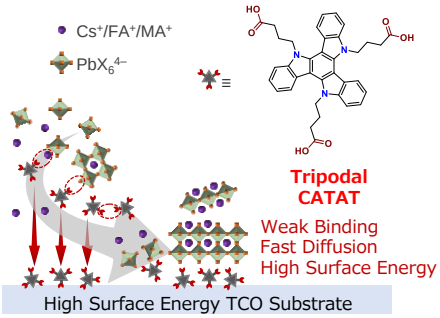

Figure 4. Tripodal **CATAT** Molecule for One-step Method.

In this presentation, our studies on multipodal molecules will be introduced in detail.

1) A. Magomedov, V. Getautis, et al., *Adv. Energy Mater.* **2018**, *8*, 1801892. 2) V. Getautis, S. Albrecht, et al., *Science* **2020**, *370*, 1300. 3) M. A. Truong, A. Wakamiya, et al., *J. Am. Chem. Soc.* **2023**, *145*, 7528. 4) M. A. Truong, A. Wakamiya, et al., *Angew. Chem., Int. Ed.* **2024**, *63*, e202412939. 5) M. A. Truong, A. Wakamiya, et al., *J. Am. Chem. Soc.* **2025**, *147*, 2797.