アカデミックプログラム［Ｂ講演］ | 21. エネルギーとその関連化学，地球・宇宙化学：口頭Ｂ講演

2025年3月28日(金) 13:00 ~ 15:30 [A]A405(第3学舎 1号館 [4階] A405)

[[A]A405-3pm] 21. エネルギーとその関連化学，地球・宇宙化学

座長：岡 伸人、久保 貴哉

英語
13:00 ~ 13:20
[[A]A405-3pm-01]
リチウム酸素二次電池における放電停止機構の電流密度依存性

〇後藤 輝海[1]、西岡 季穂[1,2]、岩瀬 和至[1,3]、向山 義治[1,4]、中西 周次[1,5] (1. 大阪大学大学院基礎工学研究科附属太陽エネルギー化学研究センター、2. 京都大学大学院工学研究科材料工学専攻、3. 東北大学多元物質科学研究所、4. 東京電機大学理工学部、5. 物質・材料研究機構エネルギー・環境材料研究センター)

英語
13:20 ~ 13:40
[[A]A405-3pm-02]
液相プラズマ法による窒素ドープ単層カーボンナノチューブ担持白金ナノ粒子触媒の合成と燃料電池への応用

〇Qiao Chen[1]、Miftakhul Huda[1]、川角 昌弥[1,2]、松尾 豊[1,2] (1. 名大院工、2. 名大未来社会)

英語
13:40 ~ 14:00
[[A]A405-3pm-03]
単層カーボンナノチューブ担持白金/窒素ドープカーボンコアシェルナノ粒子電極触媒の作製と燃料電池への応用

〇于 初陽[1]、Miftakhul Huda[1]、川角 昌弥[1,2]、松尾 豊[1,2] (1. 名大院工、2. 名大未来社会)

14:00 ~ 14:10
休憩

英語
14:10 ~ 14:30
[[A]A405-3pm-04]
電気化学的CO2還元反応におけるPdサブナノ粒子の触媒評価

〇飯塚 忠寿[1]、ATQA Augie[2]、塚本 孝政[3]、葛目 陽義[4]、今岡 享稔[1]、山元 公寿[1] (1. 科学大化生研、2. 東大院理、3. 東大生研、4. 山梨大学クリーンエネルギー研究センター)

日本語
14:30 ~ 14:50
[[A]A405-3pm-05]
ペロブスカイト酸化物への高濃度Fドーピングと酸素発生触媒への応用

〇岩瀬 和至[1]、大高 正幹[1]、本間 格[1] (1. 東北大学)

英語
14:50 ~ 15:10
[[A]A405-3pm-06]
A *m*-Terphenyl Umbrella for Fused Porphyrin Dyes toward High-Performance Dye-Sensitized Solar Cells

〇YUZHE ZHANG[1], TOMOHIRO HIGASHINO[1], HIROSHI IMAHORI[1] (1. Kyoto University)

🏷 英語

15:10 ~ 15:30

[[A]A405-3pm-07]

Development of New ITIC isomers for Non-Fullerene Acceptors in Organic Solar Cells

〇Kai Wang[1], Seihou Jinnai[1,2], Yutaka Ie[1,2] (1. SANKEN, Osaka University, 2. ICS-OTRI, Osaka University)

Current Density Dependence of Discharge Termination Mechanisms in Lithium-Oxygen Secondary Batteries

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Department of Materials Science and Engineering, Kyoto University,* [3]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,* [4]*College of Science and Engineering, Tokyo Denki University,* [5]*Research Center for Energy and Environmental Materials, NIMS*)
○Terumi Goto,[1] Kiho Nishioka,[1,2] Kazuyuki Iwase,[1,3] Yoshiharu Mukouyama,[1,4] Shuji Nakanishi[1,5]

Keywords: Lithium Oxygen Batteries; Next-generation Secondary Batteries; Oxygen Reduction Reaction

Lithium-oxygen secondary batteries (Li-O_2 batteries) have attracted attention as a next-generation secondary battery due to their high theoretical gravimetric energy density. In this system, lithium peroxide (Li_2O_2), a solid with poor electrical conductivity, forms on the positive electrode during discharge. Ideally, this Li_2O_2 should be completely decomposed via oxidation at a low charging voltage; however, in reality, the charging voltage is high, and the cycle performance and energy efficiency of Li-O_2 batteries remain low. To address this issue, it is crucial to systematically understand the formation behavior of Li_2O_2 during the discharge process. In this study, we focused on the discharge termination mechanisms. Fig. 1 shows the discharge profiles at two different current densities. At a low current density (1 µA cm^{-2}), the discharge capacity reached 50 µA h cm^{-2}. In this experiment, second discharge tests were conducted under the same conditions immediately after the first discharge termination. The second discharge at low current density ceased almost immediately. According to the conventional understanding of the discharge determination in Li-O_2 batteries, this result is interpreted as being caused by the irreversible blockage of the cathode surface by Li_2O_2 deposition. On the other hand, at high current density (50 µA cm^{-2}), the discharge capacity reached 5 µA h cm^{-2}. Notably, the first and second discharge curves at high current density overlapped, a phenomenon that cannot be explained by the conventional understanding. This observation indicates that the cathode after discharge at high current density does not remain blocked by Li_2O_2 and is, in fact, reversible. These findings reveal two distinct discharge termination mechanisms that are dependent on the current density.

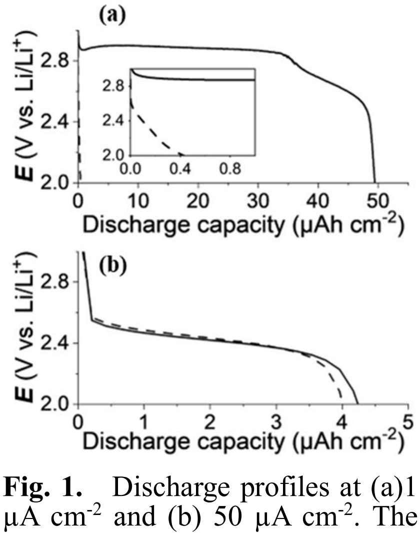


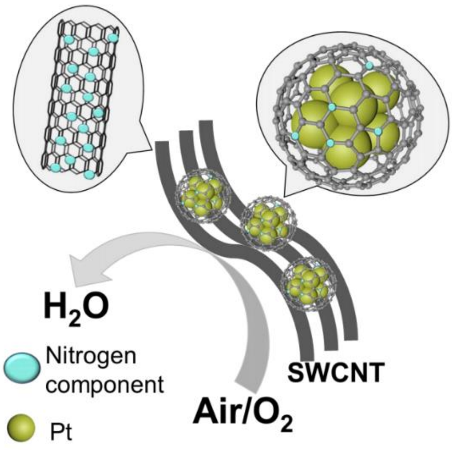
Fig. 1. Discharge profiles at (a)1 µA cm^{-2} and (b) 50 µA cm^{-2}. The solid and dashed lines show the first and second discharge, respectively.

Nitrogen-doped SWCNT-supported Pt Electrocatalysts Synthesized by Solution Plasma for Fuel Cells Application

([1]*Graduate School of Engineering, Nagoya University,* [2]*Institutes of Innovation for Future Society, Nagoya University*) ○Qiao Chen,[1] Miftakhul Huda,[1] Masaya Kawasumi,[1,2] Yutaka Matsuo[1,2]

Keywords: Single-Walled Carbon Nanotubes; Oxygen Reduction Reaction; PEM Fuel Cell; Pt Catalyst; Solution Plasma Process

Platinum (Pt)-based electrocatalysts are widely regarded as the preferred choice for the oxygen reduction reaction (ORR) in polymer electrolyte fuel cells (PEFCs). However, their limited durability remains a significant challenge. Under the typical operating conditions of the cells, Pt is exposed to the highly oxidizing environment such as high potentials and O_2 atmospheres. Long-term exposure leads to a gradual loss of electrochemical surface area (ECSA) owing to Ostwald ripening, agglomeration of Pt nanoparticles, and the corrosion of carbon supports. This permanent loss of ECSA adversely affects the performance and lifespan of PEFCs.[1] To address this issue, high-crystallinity and high-purity single-walled carbon nanotubes (SWCNTs), synthesized via enhanced direct injection pyrolytic synthesis (e-DIPS)[2] as a support through nitrogen doping pretreatment to further prepare Pt/N-SWCNT by the solution plasma (SP) method. Pt nanoparticles in the catalyst were encapsulated with nitrogen-doped carbon shells.[3]



When Pt/N-SWCNT was used as a cathode catalyst in a membrane electrode assembly (MEA), it exhibited remarkable durability, with the maximum power density decreasing by only 20.8% after the accelerated degradation test (ADT) of 16,000 cycles. Under a high-potential accelerated condition (1.0–1.5 V), the Pt/N-SWCNT-MEA demonstrated a significantly lower maximum power density loss of 39.5%, outperforming Pt/SWCNT-MEA (48.3%) and commercial Pt/C (93.2%). These findings indicate the pivotal role of SWCNTs as a robust support material and nitrogen-doped carbon shells in enhancing the stability and activity of the catalyst, thereby contributing to the superior performance of PEFCs.

1) M. Karuppannan, Y. Kim, S. Gok, E. Lee, J. Y. Hwang, J. H. Jang, O. J. Kwon, *Energy Environ. Sci.* **2019**, *12*, 2820. 2) M. Huda, T. Kawahara, J.-H. Park, M. Kawasumi, Y. Matsuo, *ACS Appl. Energy Mater.* **2023**, *6*, 12226. 3) J.-H. Park, K. Kim, X. Wang, M. Huda, Y. Sawada, Y. Matsuo, M. Kawasumi, *J. Power Sources.* **2023**, *580*, 233419.

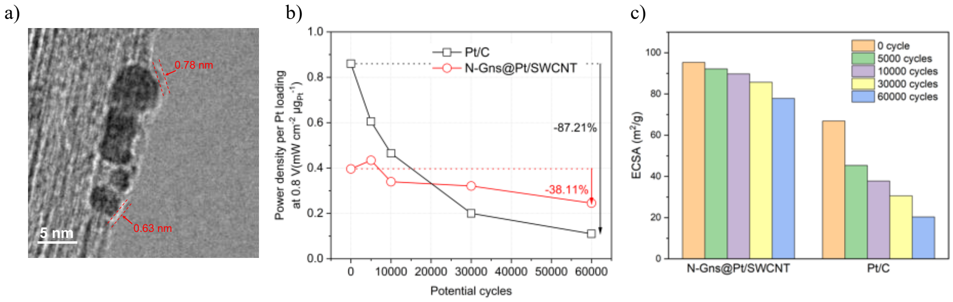
Nitrogen-doped graphene-shell-encapsulated platinum nanocatalyst supported by SWCNTs with high performance and high durability for fuel cell

([1]*Department of Chemical System Engineering, Graduate School of Engineering, Nagoya University.,* [2]*Institute of Materials Innovation, Institutes of Innovation for Future Society, Graduate School of Engineering, Nagoya University.*) ○Chuyang Yu,[1] Miftakhul Huda,[1] Masaya Kawasumi,[1, 2] Yutaka Matsuo,[1, 2]

Keywords: Nitrogen-doped graphene; SWCNTs; Solution plasma; Oxygen reduction reaction; Durability

High cost and susceptibility to corrosion of platinum-based catalysts, widely used in polymer electrolyte membrane fuel cells (PEFCs), remain major barriers to their development. The development of electrocatalysts featuring high efficiency, enhanced durability of Pt nanoparticles and more durable carbon support nanomaterials represents the trend in advancing PEMFCs device. Here, we report a nitrogen-doped graphene-shells-encapsulated platinum nanocatalysts supported by SWCNTs (N-Gns@Pt/SWCNT), featuring a core-shell structure that protects Pt nanoparticles.

DMF 6 mL, ethylene glycol 4 mL, and $H_2PtCl_6{\cdot}6H_2O$ 8wt% 100 mg were mixed and stirred, and added to the SWCNT treated by SP process.[1] The mixture dispersed by ultrasonication for 15 min was reacted in a Teflon lined autoclave at 170 °C for 8 h to synthesis the N-Gns@Pt/SWCNT.[2] N-Gns@Pt/SWCNT demonstrates remarkable durability, with an ECSA retention exceeds 80% after 60,000 ADT cycles and power density retention exceeds 60% at 0.8 V. The high chemically-durable of SWCNTs further contributes to stable performance and minimizes corrosion even under rigorous high-voltage triangular wave. At triangular wave, power density retention of N-Gns@Pt/SWCNT is more than 9 times that of commercial Pt/C. This work achieved higher durability by combining nitrogen-doped graphene with SWCNTs, offering insights for designing fuel cell catalysts with longer lifespans and lower cost. This work also provides a valuable reference for the application of SWCNTs for PEFCs.



1) J. Park, *Carbon*. **2023**, 214, 118364. 2) M. Huda, *ACS Appl. Energy Mater.* **2023**, 6, 12226−12236.

Catalytic evaluation of Pd subnanoparticle in electrochemical CO_2 reduction reaction

(*[1]Lab. for Chemistry and Life Science, Institute of Science Tokyo, [2]Graduate School of Science, The University of Tokyo, [3]Institute of Industrial Science, The University of Tokyo, [4]Clean Energy Research Center, University of Yamanashi*)

○ Tadatoshi Iitsuka,[1] Augie Aqta[2], Takamasa Tsukamoto[3], Akiyoshi Kuzume[4], Takane Imaoka[1], Kimihisa Yamamoto[1]

Keywords: *metal cluster, metal subnanoparticle, electrochemical CO_2 reduction reaction*

In recent years, the development of technologies to convert CO_2 into useful chemicals has been increasingly demanded to achieve a carbon-neutral society. Electrochemical CO_2 reduction reactions (CO_2RR) are promising methods that enable the conversion of CO_2 into CO or HCOOH under ambient conditions using renewable energy. However, suppressing the competing hydrogen evolution reaction (HER) remains a significant challenge. Pd is a catalytic element capable of converting CO_2 into CO with high Faradaic efficiency, and the relationship between its structure and CO selectivity has been extensively studied[1)]. In Pd catalysts, it is known that energetically stable terrace sites are predominant for HER, while unsaturated coordination sites such as edges and kinks are predominant for CO formation[2,3)]. Therefore, designing a Pd catalyst material consisting only of unsaturated coordination sites may allow complete suppression of HER and achieve high Faraday efficiency of CO. Metal subnanoparticles (SNPs) with a diameter of approximately 1 nm are predominantly composed of unsaturated coordination sites, making them promising catalysts for CO_2RR. However, there are no reports on the application of Pd SNP to CO_2RR, because of the difficulty of synthesizing SNPs. In this study, Pd SNP were synthesized using a dendritic polymer, phenylazomethine dendrimer (DPA-G4), as a template[4)], and their catalytic performance in CO_2RR was evaluated.

12 equivalents of $Pd(C_5H_6O_2Cl)(CH_3CN)_2BF_4$ were added to DPA-G4, allowing the accumulation of Pd complexes onto DPA-G4. Subsequently, chemical reduction with $NaEt_3BH$ was performed to synthesize Pd SNP. ADF-STEM analysis confirmed an average particle size of 0.97 ± 0.18 nm. The CO_2RR performance of Pd SNP and commercial Pd/C was evaluated using an H-cell. This presentation reports the differences in Faradaic efficiency for CO production between Pd SNP and nanoparticles.

1) T.-W. Jiang *et al.*, *J. Mater. Chem. A.,* **2024***, 12,* 21515

2) D. Gao *et al.*, *J. Am. Chem. Soc.,* **2015***, 137,* 4288.

3) W. Zhu *et al.*, *Angew. Chem. Int. Ed.*, **2018**, *57*, 11544.

4) K. Yamamoto *et al.*, *Nat. Chem.*, **2009**, *1*, 397.

ペロブスカイト酸化物への高濃度 F ドーピングと酸素発生触媒への応用

（東北大多元研 [1]・東北大環境 [2]）○岩瀬 和至 [1]・大高 正幹 [1,2]・本間 格 [1]
Wide-Range Fluorine Doping in Perovskite Oxides and Application to Oxygen Evolution Electrocatalysis ([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, [2]*Graduate School of Environmental Studies, Tohoku University*) ○Kazuyuki Iwase,[1] Masaki Ohtaka,[1,2] Itaru Honma[1]

The oxygen evolution reaction (OER) is a key anodic reaction in water electrolysis, requiring highly active catalysts composed of only abundant elements. Perovskite oxides (PVs) are promising OER catalysts due to their flexibility in designing metal elements and their compositions. Controlling the valence of metal ions in PVs has been reported to be crucial for enhancing OER activity. In this study, $BaFe_{1-x}Co_xO_{3-d}$ (BFCO, x = 0, 0.1, 0.2) was synthesized via the sol-gel method and subjected to fluoride ion (F) doping using a low-temperature process to control the valence of metal ions. Structural analysis confirmed successful F doping without significant impurity formation. Increased F doping amount particularly reduced the valence of Co ions. Evaluation of OER activity showed that F doping enhanced OER current density by up to fourfold in Co-containing PVs, highlighting the importance of controlling the valence of Co for improving OER activity.[1] Further details will be discussed in the presentation.

Keywords : Perovskite oxides, electrocatalysts, water electrolysis, fluorine doping, XAFS

電気化学的酸素発生反応(OER)は水電解のアノード反応として重要であり、安価な遷移金属から構成される高活性な OER 触媒の開発が求められている。ペロブスカイト酸化物(PV)は、金属元素とその組成の設計自由度が高く、金属イオンの価数を制御することが OER 活性の向上に重要であると報告されている。本研究では、PV として $BaFe_{1-x}Co_xO_{3-d}$ (BFCO, x = 0, 0.1, 0.2)を用い、低温プロセスによりフッ化物イオン(F)を多量にドープして金属イオンの価数を制御し、OER 活性の向上を目指した。BFCO はゾルゲル法で合成し、フッ素含有樹脂と混合後に 370 ºC で熱処理することで F ドープ PV を得た。構造解析の結果、不純物の生成をほぼ伴わずに F ドープ PV が合成されたこと、F ドープ量の増加に伴い特に Co が還元されることが確認された。OER 活性を評価したところ、Co を含む PV への F ドープにより最大で約 4 倍 OER 電流が向上した。この結果は、Co の価数制御が OER 活性向上に重要であることを示唆している。[1] 当日の発表では、構造解析および活性の詳細についてさらに議論する。

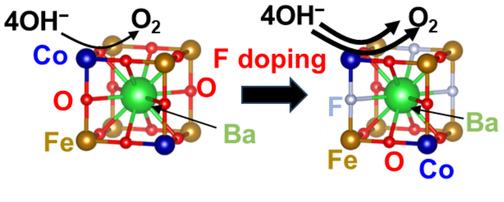


Figure. The schematic illustration of this study.

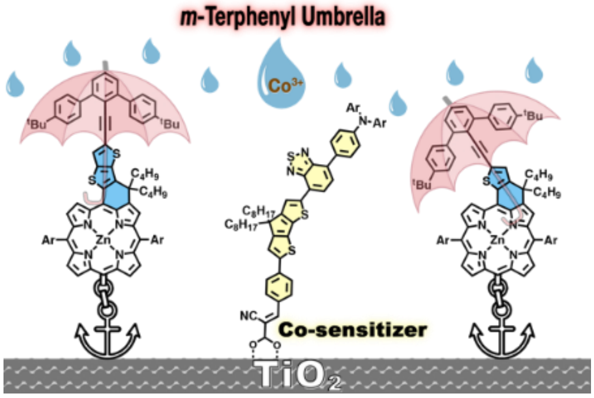
1) K. Iwase et al., Chem. Mater., *Chem. Mater.,* 35, 7, 2773–2781 (2023).

A *m*-Terphenyl Umbrella for Fused Porphyrin Dyes toward High-Performance Dye-Sensitized Solar Cells

([1]Graduate School of Engineering, Kyoto University, [2]Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, [3]Institute for Liberal Arts and Sciences (ILAS), Kyoto University) ○Yuzhe Zhang,[1] Tomohiro Higashino,[1] Issei Nishimura,[1] and Hiroshi Imahori[1,2,3]

Key words: dye-sensitized solar cells, porphyrin, *m*-terphenyl, blocking effect

Porphyrin dyes with π-extended structures, particularly those with aromatic fused designs, have garnered considerable attention as efficient sensitizers for dye-sensitized solar cells (DCCSs) because of their effectively π-extended nature and resultant excellent light-harvesting ability. However, their photovoltaic performance is often limited by high aggregation tendencies caused by strong π–π interactions and charge recombination processes. Since *m*-terphenyls can serve as effective steric protecting groups, incorporating umbrella-shaped *m*-terphenyls on top of porphyrin dyes could unlock the full potential of highly π-extended porphyrin dyes. In this study, we designed and synthesized new fused porphyrin dyes with a *m*-terphenyl group: **T-Ph**, **T-*t*BuPh**, **TT-Ph**, and **TT-*t*BuPh**. Under optimized conditions, DSSCs with **T-Ph** and **T-*t*BuPh** achieved a remarkable power conversion efficiency (PCE) of 11.5%, surpassing those with reference porphyrin dyes, **GY50** with a V-shaped diarylamino group, and **DfZnP** without a *m*-terphenyl group. More importantly, the co-sensitized DSSC using **T-*t*BuPh** and a complementary dye **XY1B** afforded the highest PCE of 12.3% ever reported for DSSCs with fused porphyrin dyes. The *m*-terphenyl umbrella effectively blocks dye aggregation on TiO_2 and charge recombination against redox shuttles, enhancing the photovoltaic performance of DSSCs with fused porphyrin dyes.



Development of New ITIC Isomers for Non-Fullerene Acceptors in Organic Solar Cells

([1]*SANKEN, Osaka University*, [2]*ICS-OTRI, Osaka University*) ○ Wang Kai,[1] Seihou Jinnai,[1,2] Yutaka Ie[1,2]

Keywords: Organic Solar Cells; n-Type Organic Semiconductors; ITIC; Electron Acceptors; Non-fullerene Acceptors

ITIC[1] is a representative non-fullerene acceptor (NFA) that has gained significant attention in OSC research due to its outstanding optoelectronic properties and flexible molecular design[2]. The molecular engineering strategies for the **ITIC** series include replacing terminal electron-accepting units, modifying electron-donating fused cores and regulating bulky side chains. Furthermore, the aggregation behaviors of molecules play a crucial role in determining the orbital energy levels of the aggregates, which in turn impacts the optoelectronic properties and OSC characteristics. Here, two types of **ITIC**-based NFA[3] (named, **im-ITI** and **io-ITIC**) with C_{2v} symmetry (Figure 1) were designed and synthesized to investigate the effect of molecular structure on the optoelectronic properties and OSC characteristics.

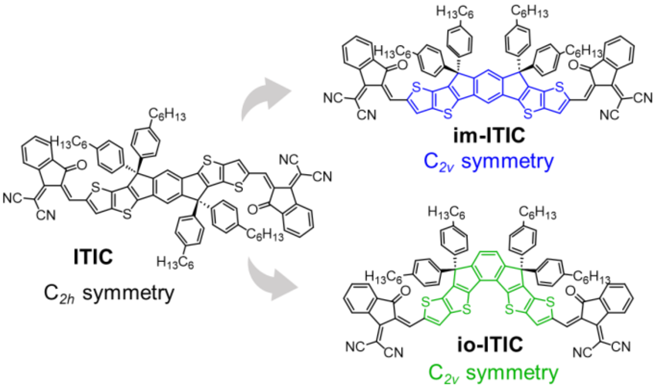


Figure 1. Molecular structures of **im-ITIC**, **io-ITIC**, and **ITIC**.

The UV-vis absorption spectra in film state of **im-ITIC**, **io-ITIC,** and **ITIC** showed maximum absorbance peaks at 637, 667 and 698 nm, respectively (Figure 2a). The OSC devices using **im-ITIC** as an acceptor and PBDB-T (CAS No. 1415929-80-4) as a donor showed a higher open-circuit voltage than that of **io-ITIC** and **ITIC** (Figure 2b) due to their different stacking modes and aggregation behaviors.

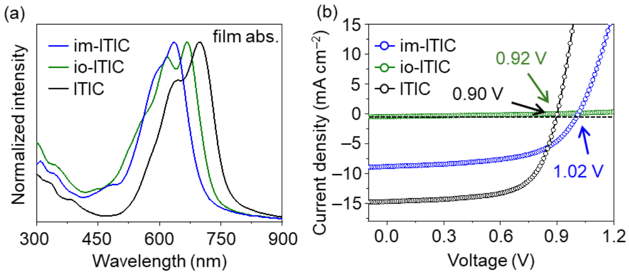


Figure 2. (a) UV-vis absorption spectra and (b) *J*–*V* curves of **im-ITIC**-, **io-ITIC**-, and **ITIC**-based OSCs.

1 Y. Z. Lin et al., *Adv. Mater.*, 2015, **27**, 1170-1174.
2 K. Wang, S. Jinnai, T. Urakami, H. Sato, M. Higashi, S. Tsujimura, Y. Kobori, R. Adachi, A. Yamakata and Y. Ie, *Angew. Chem. Int. Ed.*, 2024, e202412691.
3 K. Wang, S. Jinnai and Y. Ie, *Chem. Lett.*, 2024, **53**, upae220.