Division of Multidisciplinary Chemistry
– Molecular Aggregation Analysis –

https://www.scl.kyoto-u.ac.jp/~wakamiya/english/index.html

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Scope of Research

We design and synthesize unique electronic materials with sophisticated device applications in mind. These materials have novel solid-state aggregation structures or well-defined interface orientation that promote efficient electrical current flow or enhance device lifetime. Electronic devices based on these new materials are then evaluated using advanced measurement techniques, and the results are used to inform the next direction of the materials chemistry. We call this synergistic approach for achieving our research goals "Needs Inspired Fundamental Science".

KEYWORDS

Molecular Design and Synthesis
Functional Materials
Perovskite Solar Cells
Molecular Aggregation
Semiconductors

Selected Publications

Liu, J.; Ozaki, M.; Yakumaru, S.; Handa, T.; Nishikubo, R.; Kanemitsu, Y.; Saeki, A.; Murata, Y.; Murdey, R.; Wakamiya, A., Lead-Free Solar Cells Based on Tin Halide Perovskite Films with High Coverage and Improved Aggregation, *Angew. Chem. Int. Ed.*, **57,** 13221-13225 (2018).

Truong, M. A.; Lee, J.; Nakamura, T.; Seo, J.-Y.; Jung, M.; Ozaki, M.; Shimazaki, A.; Shioya, N.; Hasegawa, T.; Murata, Y.; Zakeeruddin, S. M.; Gratzel, M.; Murdey, R.; Wakamiya, A., Influence of Alkoxy Chain Length on the Properties of Two-Dimensionally Expanded Azulene Core-Based Hole-Transporting Materials for Efficient Perovskite Solar Cells, *Chem. Eur. J.*, **25,** 6741-6752 (2019).

Ozaki, M.; Shimazaki, A.; Jung, M.; Nakaike, Y.; Maruyama, N.; Yakumaru, S.; Rafieh, A. I.; Sasamori, T.; Tokitoh, N.; Ekanayake, P.; Murata, Y.; Murdey, R.; Wakamiya, A., A Purified, Solvent-Intercalated Precursor Complex for Wide Process Window Fabrication of Efficient Perovskite Solar Cells and Modules, *Angew. Chem. Int. Ed.*, **58,** 9389-9393 (2019).

Nakamura, T.; Yakumaru, S.; Truong, M. A.; Kim, K.; Liu, J.; Hu, S.; Otsuka, K.; Hashimoto, R.; Murdey, R.; Sasamori, T.; Kim, H. D.; Ohkita, H.; Handa, T.; Kanemitsu, Y.; Wakamiya, A., Sn(IV)-free Tin Perovskite Films Realized by in situ Sn(0) Nanoparticle Treatment of the Precursor Solution, *Nat. Commun.*, **11,** 3008 (2020).

Nishimura, H.; Okada, I.; Tanabe, T.; Nakamura, T.; Murdey, R.; Wakamiya, A., Additive-free Cost-Effective Hole-Transporting Materials for Perovskite Solar Cells Based on Vinyl Triarylamines, *ACS Appl. Mater. Interfaces*, **12,** 32994-33003 (2020).

Sn(IV)-Free Tin Perovskite Films Realized by in situ Sn(0) Nanoparticle Treatment of the Precursor Solution

The toxicity of lead perovskite hampers the commercialization of perovskite-based photovoltaics. While tin perovskite is a promising alternative, the facile oxidation of tin(II) to tin(IV) causes a high density of defects, resulting in lower solar cell efficiencies. Here, we show that tin(0) nanoparticles in the precursor solution can scavenge tin(IV) impurities, and demonstrate that this treatment leads to effectively tin(IV)-free perovskite films with strong photoluminescence and prolonged decay lifetimes. These nanoparticles are generated by the selective reaction of a dihydropyrazine derivative with the tin(II) fluoride additive already present in the precursor solution. Using this nanoparticle treatment, the power conversion efficiency of tin-based solar cells reaches 11.5%, with an open-circuit voltage of 0.76 V. Our nanoparticle treatment is a simple and broadly effective method that improves the purity and electrical performance of tin perovskite films.

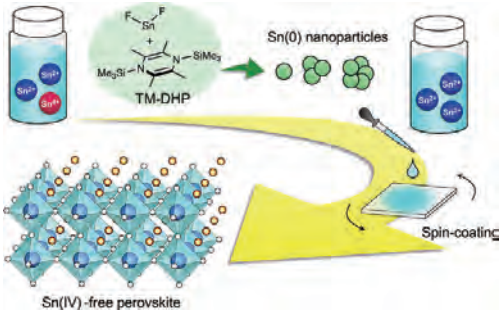

Figure 1. Schematic illustration of the Sn(IV) scavenging method to fabricate Sn(IV)-free perovskite films.

Hole-Transporting Polymers Containing Partially Oxygen-Bridged Triphenylamine Units and Their Application for Perovskite Solar Cells

A series of polymers composed of partially oxygen-bridged triphenylamine units was successfully synthesized by Suzuki-Miyaura or Migita-Kosugi-Stille cross coupling reactions. In addition to the polymer with directly connected triphenylamine units, **P1**, different π-spacers, were introduced into the polymer main chains including *m*-benzene, **P2**, *p*-benzene, **P3**, and bithiophene, **P4**. Photoelectron yield spectroscopy (PYS) results showed that the highest occupied molecular orbitals of these polymers lie above the valence bands of typical metal halide perovskites, suggesting efficient hole extraction from the perovskite. When used as hole-transporting materials in perovskite solar cells, the maximum power conversion efficiency (PCE) of **P1–P4** reached 7.9% with LiTFSI additive, while the device of **P1** and **P4** without additive showed better PCE of 12.1% and 11.1%, respectively.

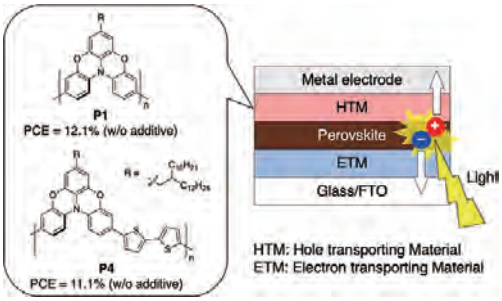

Figure 2. Development of hole-transporting polymers containing partially oxygen-bridged triphenylamine units.

Additive-Free, Cost-Effective Hole-Transporting Materials for Perovskite Solar Cells Based on Vinyl Triarylamines

A series of cost-effective hole-transporting materials (TOP-HTMs) for perovskite solar cells (PSCs) was designed and synthesized. The molecules, composed of multiple 4,4′-dimethoxytriphenylamines linked to a benzene core via *trans*-vinylene units, can be manufactured from inexpensive materials through a simple synthetic route. The photophysical, electrochemical, and thermal properties, as well as hole mobilities were strongly influenced by the position and number of vinyl triarylamine substituents on the core benzene ring. $CH_3NH_3PbI_3$-based solar cells using the X-shaped TOP-HTM **3** with additives gave a high power conversion efficiency of 17.5% (forward scan) / 18.6% (reverse scan). Crucially, TOP-HTMs gave high working device efficiency without the need for conduction-enhancing additives. The power conversion efficiency for the device with additive-free TOP-HTM **3** was 16.0% (forward scan) / 16.6% (reverse scan). Device stability is also enhanced and is superior to the reference HTM, 2,2′,7,7′-Tetrakis (*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD).

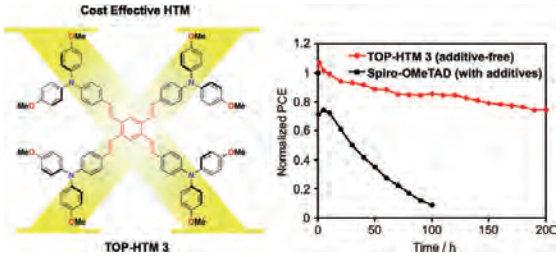

Figure 3. Chemical structure of X-shaped TOP-HTM **3** and the enhanced stability of perovskite solar cell device.