

# Division of Multidisciplinary Chemistry – Molecular Aggregates –

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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

Molecular Aggregation

Functional Materials

Semiconductors

Perovskite Solar Cells

## Recent Selected Publications

Hu, S.; Zhao, P.; Nakano, K.; Oliver, R. D. J.; Pascual, J.; Smith, J. A.; Yamada, T.; Truong, M. A.; Murdey, R.; Shioya, N.; Hasegawa, T.; Ehara, M.; Johnston, M. B.; Tajima, K.; Kanemitsu, Y.; Snaith, H. J.; Wakamiya, A., Synergistic Surface Modification of Tin-Lead Perovskite Solar Cells, *Adv. Mater.*, **35**, 2208320 (2023).

Truong, M. A.; Funasaki, T.; Ueberricke, L.; Nojo, W.; Murdey, R.; Yamada, T.; Hu, S.; Akatsuka, A.; Sekiguchi, N.; Hira, S.; Xie, L.; Nakamura, T.; Shioya, N.; Kan, D.; Tsuji, Y.; Iikubo, S.; Yoshida, H.; Shimakawa, Y.; Hasegawa, T.; Kanemitsu, Y.; Suzuki, T.; Wakamiya, A., Tripodal Triazatruxene Derivative as a Face-On Oriented Hole-Collecting Monolayer for Efficient and Stable Inverted Perovskite Solar Cells, *J. Am. Chem. Soc.*, **145**, 7528-7539 (2023).

Tan, T.; Nakamura, T.; Murdey, R.; Hu, S.; Truong, M. A.; Wakamiya, A.,  $\text{BAR}_2$ -Bridged Azafulvene Dimers with Tunable Energy Levels for Photostable Near-Infrared Dyes, *Chem. Eur. J.*, **29**, e202300529 (2023).

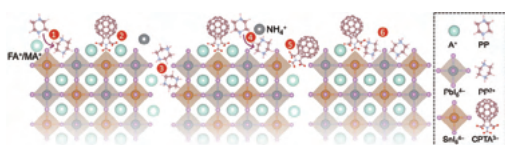
Hashimoto, R.; Nakamura, T.; Truong, M. A.; Murdey, R.; Wakamiya, A., Effects of Electron-Accepting Substituents on the Fluorescence of Oxygen-Bridged Triarylamine, *Dyes Pigm.*, **215**, 111281 (2023).

Ohashi, N.; Kaneko, R.; Sakai, C.; Wasai, Y.; Higuchi, S.; Yazawa, K.; Tahara, H.; Handa, T.; Nakamura, T.; Murdey, R.; Kanemitsu, Y.; Wakamiya, A., Bilayer Indium Tin Oxide Electrodes for Deformation-Free Ultrathin Flexible Perovskite Solar Cells, *Sol. RRL*, **7**, 2300221 (2023).

Liu, W.; Hu, S.; Pascual, J.; Nakano, K.; Murdey, R.; Tajima, K.; Wakamiya, A., Tin Halide Perovskite Solar Cells with Open-Circuit Voltages Approaching the Shockley-Queisser Limit, *ACS Appl. Mater. Interfaces*, **15**, 32487-32495 (2023).

## Synergistic Surface Modification of Tin–Lead Perovskite Solar Cells

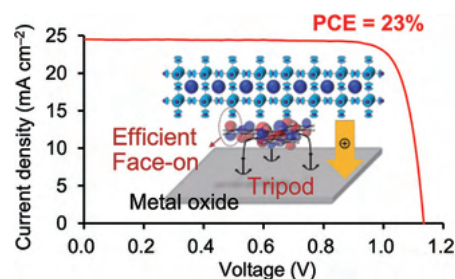
Interfaces in thin-film photovoltaics play a pivotal role in determining device efficiency and longevity. In this work, the top surface treatment of mixed tin–lead ( $\approx 1.26$  eV) halide perovskite films for p–i–n solar cells is studied. Charge extraction is promoted by treating the perovskite surface with piperazine. This compound reacts with the organic cations at the perovskite surface, modifying the surface structure and tuning the interfacial energy level alignment. In addition, the combined treatment with C<sub>60</sub> pyrrolidine tris-acid (CPTA) reduces hysteresis and leads to efficiencies up to 22.7%, with open-circuit voltage values reaching 0.90 V,  $\approx 92\%$  of the radiative limit for the bandgap of this material. The modified cells also show superior stability, with unencapsulated cells retaining 96% of their initial efficiency after >2000 h of storage in N<sub>2</sub> and encapsulated cells retaining 90% efficiency after >450 h of storage in air. Intriguingly, CPTA preferentially binds to Sn<sup>2+</sup> sites at film surface over Pb<sup>2+</sup> due to the energetically favored exposure of the former, according to first-principles calculations. This work provides new insights into the surface chemistry of perovskite films in terms of their structural, electronic, and defect characteristics and this knowledge is used to fabricate state-of-the-art solar cells.<sup>1)</sup>



**Figure 1.** Surface modification of tin–lead perovskite films with piperazine and CPTA.

## Tripodal Triazatruxene Derivative as a Face-On Oriented Hole-Collecting Monolayer for Efficient and Stable Inverted Perovskite Solar Cells

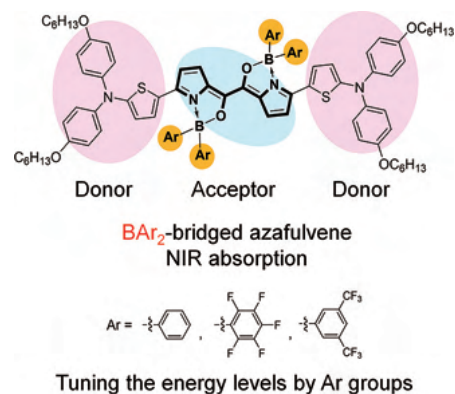
Hole-collecting monolayers have drawn attention in perovskite solar cell research due to their ease of processing, high performance, and good durability. Since molecules in the hole-collecting monolayer are typically composed of functionalized  $\pi$ -conjugated structures, hole extraction is expected to be more efficient when the  $\pi$ -cores are oriented face-on with respect to the adjacent surfaces. However, strategies for reliably controlling the molecular orientation in monolayers remain elusive. In this work, multiple phosphonic acid anchoring groups were used to control the molecular orientation of a series of triazatruxene derivatives chemisorbed on a transparent conducting oxide electrode surface. Using infrared reflection absorption spectroscopy and metastable atom electron spectroscopy, we found that multipodal derivatives align face-on to the electrode surface, while the monopodal counterpart adopts a more tilted configuration. The face-on orientation was found to facilitate hole extraction, leading to inverted perovskite solar cells with enhanced stability and high-power conversion efficiencies up to 23.0%.<sup>2)</sup>



**Figure 2.** Triazatruxene-based tripodal hole collecting monolayer for inverted perovskite solar cells.

## BAR<sub>2</sub>-Bridged Azafulvene Dimers with Tunable Energy Levels for Photostable Near-Infrared Dyes

Organic dyes with strong absorption in the near-infrared (NIR) region are potentially useful in medical applications, such as tumor imaging and photothermal therapy. In this work, new NIR dyes combining BAR<sub>2</sub>-bridged azafulvene dimer acceptors with diarylaminothienyl donors in a donor–acceptor–donor configuration were synthesized. Surprisingly, it was found that in these molecules the BAR<sub>2</sub>-bridged azafulvene acceptor adopts a 5-membered, rather than 6-membered ring structure. The influence of the aryl substituents on the HOMO and LUMO energy levels of the dye compounds was assessed from electrochemical and optical measurements. Strong electron-withdrawing fluorinated substituents (Ar = C<sub>6</sub>F<sub>5</sub>, 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) lowered the HOMO energy while preserving the small HOMO–LUMO energy gap, resulting in promising NIR dye molecules that combine strong absorption bands centered around 900 nm with good photostability.<sup>3)</sup>



**Figure 3.** BAR<sub>2</sub>-bridged azafulvene dimer for photostable near-infrared dyes.

### References

- 1) S. Hu, P. Zhao, K. Nakano, R. D. J. Oliver, J. Pascual, J. A. Smith, T. Yamada, M. A. Truong, R. Murdey, N. Shioya, T. Hasegawa, M. Ehara, M. B. Johnston, K. Tajima, Y. Kanemitsu, H. J. Snaith, A. Wakamiya, *Adv. Mater.*, **35**, 2208320 (2023).
- 2) M. A. Truong, T. Funasaki, L. Ueberricke, W. Nojo, R. Murdey, T. Yamada, S. Hu, A. Akatsuka, N. Sekiguchi, S. Hira, L. Xie, T. Nakamura, N. Shioya, D. Kan, Y. Tsuji, S. Iikubo, H. Yoshida, Y. Shimakawa, T. Hasegawa, Y. Kanemitsu, T. Suzuki, A. Wakamiya, *J. Am. Chem. Soc.*, **145**, 7528–7539 (2023).
- 3) T. Tan, T. Nakamura, R. Murdey, S. Hu, M. A. Truong, A. Wakamiya, *Chem. Eur. J.*, **29**, e202300529 (2023).