Development of Multipodal Hole-Collecting Monolayer Materials for Perovskite Solar Cells

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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.

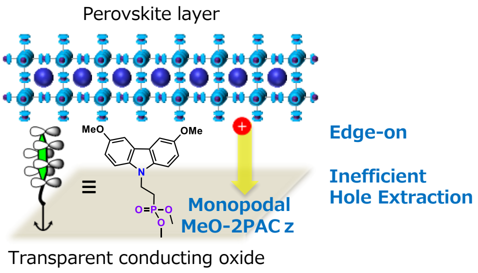

Figure 1. Conventional Monopodal Monolayer Materials.

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,

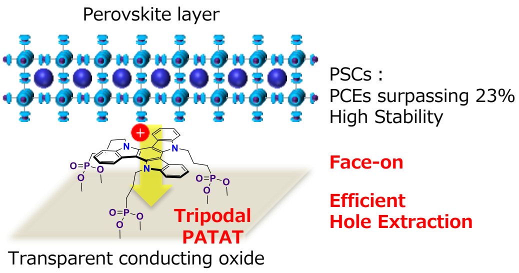

Figure 2. Tripodal **PATAT** Molecule.

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.

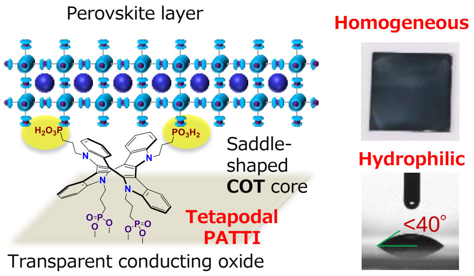

Figure 3. Tetrapodal **PATTI** Molecule.

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.

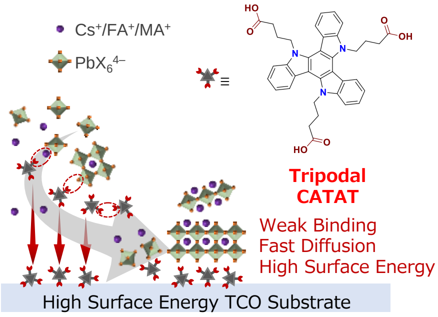

Figure 4. Tripodal **CATAT** Molecule for One-step Method.

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

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