Novel eco-friendly electrochemical reaction can synthesize useful semiconductor materials

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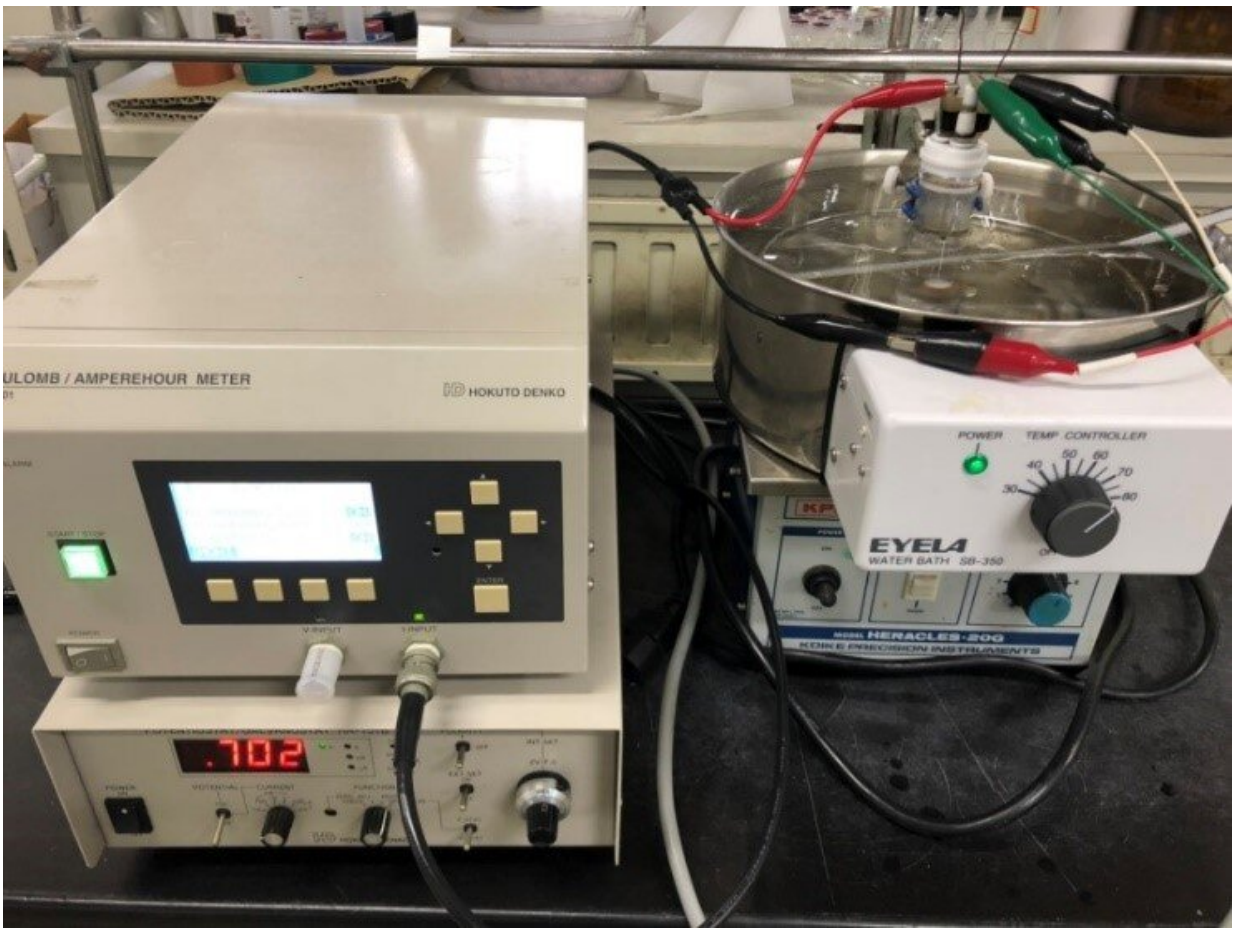

Electrochemical setup for the synthesis of thienoacene derivatives. Credit: 2020 Okayama University

Organic solar cells have a variety of applications in the field of electronics, especially in the development of novel electronic devices like wearable devices. Often, these batteries are composed of organic semiconductor molecules, which are light and robust. Thus, finding novel strategies for the development of these semiconductor molecules has been the goal of many scientists globally. But usually, synthesizing these molecules involves the use of expensive rare metal catalysts. Not only does this result in a high manufacturing cost, but the possibility of the metal catalysts being contaminated makes the process challenging.

To this end, in a new study published in *Angewandte Chemie International Edition*, a research group at Okayama University, including Professor Seiji Suga and Associate Professor Koichi Mitsudo, developed a novel reaction system to synthesize thienoacene derivatives—key building blocks in organic semiconductor synthesis. The scientists focused on constructing carbon-sulfur (C-S) bonds through organic electrolysis, which is an environment-friendly reaction. Prof Suga explains, "We focused on C-S bonds, as they are abundant and significant in the field of pharmaceuticals and materials science, such as in certain antidepressant and antifungal medications."

Conventionally, C-S bonds are constructed via a method called "transition metal-catalyzed cross-coupling," which requires the use of rare metal catalysts. This makes the reaction expensive and, thus, infeasible. Thus, in this study, the scientists focused on a different approach, called "electrochemical carbon-heteroatom bond formation," which is an eco-friendly reaction requiring mild conditions. Although several novel electrochemical carbon-heteroatom coupling reactions have been reported in the past, these reactions had never been used to synthesize thienoacenes until now. Prof Suga says, "Over the past several years, we were interested in the development of new methods for thienoacene synthesis, acene derivatives that have a good track record in organic electrochemistry and are attractive candidates for useful organic

materials."

Having established the basis of their study, the scientists then dug deeper to find novel electrochemical methods for thienoacene synthesis. They found that the desired C-S bond formation occurred smoothly in the presence of a "bromide" ion, which acts as a powerful promoter of the reaction. Using this strategy, the scientists successfully synthesized types of thienoacene derivatives called the "π-expanded thienoacene derivatives." Interestingly, this study is the first to report successful C-S bond formation for the synthesis of thienoacene derivatives. Prof Suga explains, "Our study was the first to report an electro-oxidative dehydrogenative reaction to produce C-S bonds for thienoacenes. We found that bromide ion, which catalytically promotes the reaction as a halogen mediator, is essential to the reaction."

This study offers hope that, in the future, organic semiconductor molecules can be produced using a cost-efficient technique, without the need to use expensive metal catalysts. Prof Suga concludes, "The key to this research lies in the method of 'electrochemical synthesis,' which is a clean and renewable source of energy." Through these findings, the scientists at Okayama University hope to achieve sustainable organic synthesis with minimal impact on the environment. Thus, this study is also a significant step towards achieving the UN sustainable development goals and hence promoting a better future for humanity.

More information: Koichi Mitsudo et al, Electrochemical Synthesis of Thienoacene Derivatives: Transition-Metal-Free Dehydrogenative C–S Coupling Promoted by a Halogen Mediator, *Angewandte Chemie International Edition* (2020). DOI: 10.1002/anie.202001149

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