

# Report for Interdisciplinary research startup

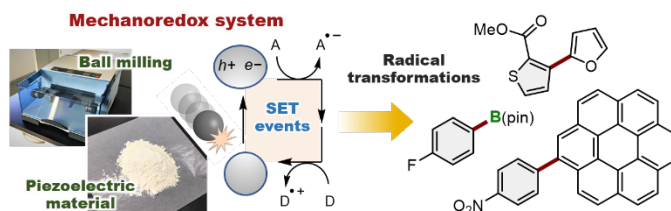
1. **Name of project leader:** Koji Kubota

2. **Project title:** 固相反応系を用いた新反応開発融合研究 / Development of new solid-state organic reactions through collaborative researches

## 3. Report

In this year, in order to launch the fusion research on the development of new solid-state organic reactions in the ICRéDD, experimental investigations that would become the seeds of future collaborative researches with calculation and information scientists was conducted. The startup budget was primarily used to purchase ball milling equipment, as well as glassware and chemical reagents needed for chemical experiments.

The development of new solid-state reactions using mechanical energy as a driving force was targeted as a seed project for future fusion research. As a result, we succeeded for the first time in the development of the mechanoredox system, a new redox reaction driven by the mechanical impact generated by a ball mill (**Kubota, K.\*; Ito, H.\* et al. *Science* 2019, 366,**

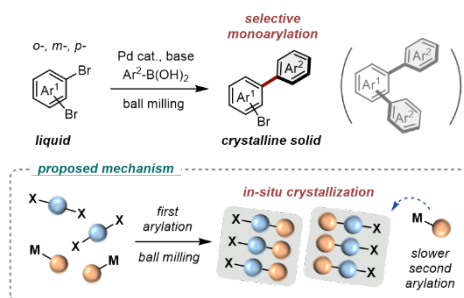


**Kubota, K.\*; Ito, H.\* et al. *Science* 2019, 366, 1500.**

1500.). In this catalytic system, the agitation of piezoelectric materials via ball milling generates temporarily highly polarized particles that can act as strong reductants to transfer electrons to small organic molecules, followed by oxidative quenching of a donor, thus inducing the selective formation of bonds in a manner analogous to photoredox catalysis. By utilizing this new solid-state redox reaction using ball milling, C-H arylation and borylation of hardly soluble compounds, which could not be applied by a conventional photoredox catalysis, with aryldiazonium salts were achieved. The present mechanoredox reactions can be carried out on gram scale without organic solvents in air, and do not require special operating conditions. This operational simplicity suggests that the present approach may complement existing photoredox transformations in a practical and environmentally friendly manner. In the next year, we will aim to clarify the detailed mechanism and improve the efficiency through collaborative research with computational and information scientists in the ICRéDD.

We have also discovered selective mechanochemical monoarylation reactions of unbiased dibromoarenes using *in situ* crystallization (**Kubota, K.\*; Ito, H.\* et al. *J. Am. Chem. Soc.* 2020, 142, 9884.**).

Suzuki–Miyaura cross-coupling reactions of unbiased dibromoarenes in solution tend to provide a mixture of mono- and diarylated products. The selective trend toward monoarylation is mostly likely derived from the fact that the liquid substrate is more reactive than the solid substrate under solvent-free mechanochemical conditions. This work has been selected as a supplementary cover art in the *Journal of the American Chemical Society*. To probe the mechanism, we are currently working on the construction of a mathematical model by collaboration with Associate Professor Dr. Tetsuya Yamamoto in the ICRéDD.



**Kubota, K.\*; Ito, H.\* et al. *J. Am. Chem. Soc.* 2020, 142, 9884.**

## 4. Research achievements

- 1) **Koji Kubota**, Tamae Seo, Katsumasa Koide, Yasuchika Hasegawa, Hajime Ito, “Olefin-accelerated C-N cross-coupling in the solid-state.” ACS Fall 2019 National Meeting and Exposition 2019 (oral presentation), San Diego Convention Center, San Diego, US, August 25-29th, 2019.
- 2) **Koji Kubota** “Mechano-redox activation: arylation and borylation promoted by mechanical force.” The 14<sup>th</sup> International Conference on Cutting-Edge Organic Synthesis in Asia (poster presentation), Hilton Village, Niseko, Japan, September 26-29th, 2019. [ACP Lecture Ship Award from Singapore]
- 3) **Koji Kubota**, Yadong Pang, Akira Miura, and Hajime Ito “Development of mechanoredox system using ball milling and piezoelectric materials” The 100th CSJ Annual Meeting, 1E3-09 (oral presentation), Noda Campus, Tokyo University of Science, Chiba, Japan, March 22th, 2020.