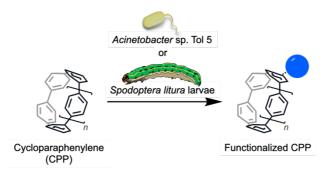
## Functionalization of cycloparaphenylene by biocatalysts

(<sup>1</sup>Research Center for Materials Science, Nagoya University, <sup>2</sup>Graduate School of Engineering, Nagoya University, <sup>3</sup>Graduate School of Science, Nagoya University, <sup>4</sup>Institute of Transformative Bio-Molecules (WPI-ITbM)) O Atsushi Usami<sup>1</sup>, Kazuma Amaike<sup>1</sup>, Katsutoshi Hori<sup>2</sup>, Kenichiro Itami<sup>3,4</sup>

Keywords: Molecular Nanocarbons, Cycloparaphenylene, Biotransformation, Biocatalysts

Molecular nanocarbons, nanometer-sized carbon materials composed of polycyclic aromatic hydrocarbons, have various physical properties and are applicable to materials chemistry.<sup>1</sup> Recently, some molecular nanocarbons have been revealed to have new properties and applicability through functionalization-based structural modifications.<sup>2</sup> However, because the molecular nanocarbon that can be regioselective functionalized is limited, there is still a requirement for a universal method to break the status quo.

We have recently focused on a biotransformation reaction, known as a highly regioselective transformation reaction, as a new way to functionalize molecular nanocarbon derivatives. This represents a green process that can be used to realize the production of chemicals that are inaccessible by traditional organic synthesis. Biocatalysts we chosen are two organisms that are resistant to various organic compounds. One is a toluene-degrading Gramnegative bacterium *Acinetobacter* sp. Tol 5, and the other is a polyphagous insect, *Spodoptera litura* larvae (Lepidoptera, Noctuidae).<sup>3,4</sup> In this study, the C-H bond functionalization of cycloparaphenylene and its derivatives, the shortest sidewall segment of carbon nanotubes, were investigated by biocatalysts.



1) a) Cheung, Y. K.; Watanabe, K.; Segawa, Y.; Itami, K. *Nat. Chem.* **2021**, *13*, 255. b) Matsuoka, W.; Ito, H.; Sarlah, D.; Itami, K. *Nat. Commun.* **2021**, *12*, 3940. c) Segawa, Y.; Kuwayama, M.; Hijikata, Y.; Fushimi, M.; Nishihara, T.; Pirillo, J.; Shirasaki, J.; Kubota, N.; Itami, K. *Science* **2019**, *365*, 272. d) Povie, G.; Segawa, Y.; Nishihara, T.; Miyauchi, Y.; Itami K. *Science* **2017**, *356*, 172.

2) a) Nagase, M.; Kato, K.; Yagi, A.; Segawa, Y.; Itami, K. *Beilstein J. Org. Chem.* **2020**, *16*, 391. b) Kubota, N.; Segawa, Y.; Itami, K. J. Am. Chem. Soc. **2015**, *137*, 1356.

3) a) Hori, K.; Yamashita, S.; Ishii, S.; Kitagawa, M.; Tanji, Y.; Unno, H. J. Chem. Engineer. Jpn. 2001,

34, 1120. b) Usami, A.; Ishikawa, M.; Hori, K. Biosci. Biotechnol. Biochem. 2018, 82, 2012.

4) Marumoto, S.; Okuno, Y.; Miyamoto, Y.; Miyazawa, M. J. Mol. Catal., B Enzym. 2015, 115, 160.