# Development of Low-Temperature Pd/Ag Dual-Catalytic Direct Arylation Polymerization for the Sustainable Synthesis of a Library of Donor−Acceptor Conjugated Polymers

Hwangseok Kim (Group of Prof. Tae-Lim Choi)

Department of Materials, ETH Zürich, Zürich 8093, Switzerland

Donor−acceptor conjugated polymers (D−A CPs) represent a highly promising class of materials for advanced organic electronic applications due to low bandgap and excellent charge carrier mobilities. Despite their advantages, conventional cross-coupling methods for preparing D−A CPs lack sustainability. Over the last two decades, direct arylation polymerization (DArP) has emerged as a greener alternative by removing the need for transmetalation agents. However, the harsh conditions typically required for C−H activation in DArP remain a significant challenge, constraining the precision and broader application of polymers. In this study, we present a sustainable and versatile Pd/Ag dual-catalyzed DArP methodology that operates efficiently under mild conditions even including room temperature, resulting in CPs with minimal structural defects. Initially, we confirmed that various electron-deficient acceptor substrates, differing in electronic characteristics and acidity (p$K_a$), underwent effective concerted-metalation-deprotonation (CMD) facilitated by Ag catalysis, followed by highly selective Pd-catalyzed C−C coupling at low temperatures. Utilizing this dual-catalytic approach, we successfully synthesized diverse libraries of both D−A and A−A CPs from acceptor monomers featuring C−H bonds and corresponding aryl halides. Remarkably, polymerization occurred effectively at temperatures (ranging from 25 °C to 70 °C) using eco-friendly solvents such as *p*-cymene. Notably, D−A conjugated polymers synthesized via this Pd/Ag dual-catalytic DArP exhibited superior structural regularity and thereby enhanced crystallinity. Consequently, these materials showed significantly improved performances in organic electronic devices compared to polymers obtained through traditional synthetic routes. Specifically, ambipolar organic field-effect transistors (OFETs) exhibited electron mobilities as high as 0.80 $cm^2 V^{-1} s^{-1}$, and complementary metal-oxide semiconductor (CMOS) inverters demonstrated remarkable gain values reaching up to 102.

