International Research Center for Elements Science
– Organometallic Chemistry –

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Scope of Research

This laboratory aims to establish new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using experimental methods such as spectroscopy and kinetic techniques, as well as theoretical methods. The research subjects include: 1) development of novel organotransition metal systems for catalysis based on precise ligand design, and 2) preparation of π-conjugated polymers using direct arylation.

KEYWORDS
Transition Metal Complex
Homogeneous Catalyst
Reaction Mechanism
Low-coordinate Phosphorus Ligand
π-Conjugated Polymer

Selected Publications

Wakioka, M.; Nakamura, Y.; Montgomery, M.; Ozawa, F., A Remarkable Ligand Effect of P(2-$MeOC_6H_4$)$_3$ on Palladium-Catalyzed Direct Arylation, *Organometallics*, **34,** 198-205 (2015).

Iizuka, E.; Wakioka, M.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Effective Prevention of Structural Defects Using Diamines, *Macromolecules*, **49,** 3310-3317 (2016).

Wakioka, M.; Takahashi, R.; Ichihara, N.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Highly Selective Synthesis of π-Conjugated Polymers with Diketopyrrolopyrrole Units, *Macromolecules*, **50,** 927-934 (2017).

Wakioka, M.; Ozawa, F., Highly Efficient Catalysts for Direct Arylation Polymerization (DArP), *Asian J. Org. Chem.*, **7,** 1206-1216 (2018).

Wakioka, M.; Morita, H.; Ichihara, N.; Saito, M.; Osaka, I.; Ozawa, F., Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Synthesis of Donor–Acceptor Polymers Containing Unsubstituted Bithiophene Units, *Macromolecules*, **53,** 158-164 (2020).

Mixed-Ligand Approach to Palladium-Catalyzed Direct Arylation Polymerization: Synthesis of Donor–Acceptor Polymers Containing Unsubstituted Bithiophene Units

The combined use of P(2-MeOC$_6$H$_4$)$_3$ (**L1**) and TMEDA as ligands effectively prevents defect formation in palladium-catalyzed direct arylation polymerization (DArP) to give donor-acceptor type alternating copolymers (DA polymers) with unsubstituted 2,2'-bithiophene units (Figure 1). When only **L1** is used as the ligand, the reaction of **1a-Br** with 2,2'-bithiophene (**2-H**) in toluene at 100 °C forms a notable amount of insoluble materials via branching and cross-linking. In contrast, in the presence of **L1** and TMEDA, the formation of insoluble materials is completely suppressed, and poly(**1a**-*alt*-**2**) with well-controlled structure and high molecular weight is obtained (M_n = 88,100). Similarly, the reaction of **1b-Br** with **2-H** in toluene at 110 °C forms poly(**1b**-*alt*-**2**) with M_n = 43,800. The resulting polymers function as good components of bulk-heterojunction type organic solar cells (OSCs) using PC$_{71}$BM. In particular, poly(**1b**-*alt*-**2**) exhibits the best performance among DArP polymers reported so far (power conversion efficiency (PCE) = 9.0(1)%).

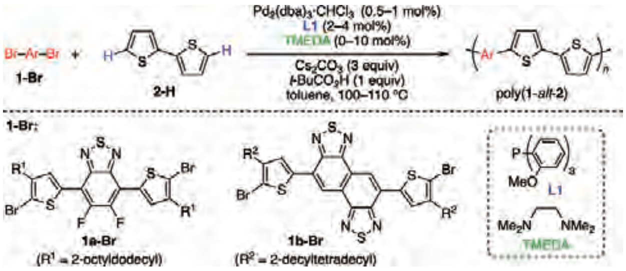

Figure 1. DArP synthesis of DA polymers containing bithiophene units.

Donor–Acceptor Polymers Containing 4,8-Dithienylbenzo[1,2-*b*:4,5-*b'*]dithiophene for Organic Solar Cells via Highly Selective Direct Arylation Polymerization

As shown above, recently, we have developed a highly selective catalyst that produces donor–acceptor-type alternating copolymers (DA polymers) with well-controlled structure via direct arylation polymerization (DArP). This method, however, often forms branching and cross-linking defects via undesirable C–H bond activation. These defects negatively impact device performance. In this new study, we the mixed-ligand catalyst shown above for the synthesis of DA polymers containing 4,8-dithienylbenzo[1,2-*b*:4,5-*b'*]dithiophene (DTBDT) units, which are known to function as excellent donors in DA polymers. The reaction of **3-Br** and **4-H** gives a DTBDT-containing DA polymer (poly(**3**-*alt*-**4**)$^{\mathrm{DArP}}$) having a well-controlled structure as it has homocoupling defects of 2.0%, which is much smaller than those of 14.8% for the Migita–Stille product (poly(**3**-*alt*-**4**)$^{\mathrm{Stille}}$). poly(**3**-*alt*-**4**)$^{\mathrm{DArP}}$ functions as a good component of bulk-heterojunction type OSC using a non-fullerene acceptor (power conversion efficiency (PCE) up to 9.9%). The photovoltaic performance for poly(**3**-*alt*-**4**)$^{\mathrm{DArP}}$ is comparable to that for poly(**3**-*alt*-**4**)$^{\mathrm{Stille}}$ (PCE up to 9.8%).

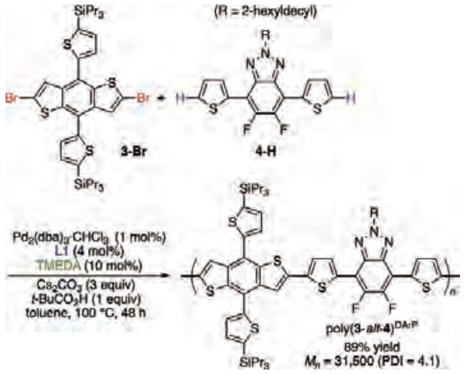

Figure 2. DArP synthesis of DA polymers containing 4,8-dithienylbenzo[1,2-*b*:4,5-*b'*]dithiophene units.

Synthesis and Properties of T-Shaped π-Conjugated Polymers

π-Conjugated polymers including poly(3-hexylthiophene) (P3HT) have attracted much attention due to their solution processability and good mechanical properties, which allow easy access to the next generation of large-area devices such as organic solar cells (OSCs) and perovskite solar cells (PSCs). To improve the performance of these devices, the π-conjugated polymers should adopt face-on orientation to the substrate, since the charges are generally transported through the intermolecular overlap of π-orbitals. Although a variety of polymers that exhibit face-on orientation have been found, the guiding principles for controlling the orientation of polymers have not yet been established. In this study, we examined T-shaped π-conjugated polymers composed of a thiazole-fused benzothiadiazole (TBT) core and three P3HT side-chains (**T-10** and **T-20**). We found that this molecular geometry could prevent the edge-on orientation and cause face-on orientation, as confirmed by 2D-GIXD.

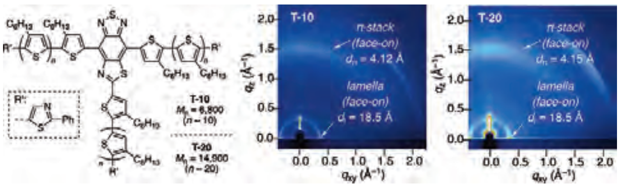

Figure 3. 2D-GIXD patterns of T-shaped π-conjugated polymers (**T-10** and **T-20**) in thin film.