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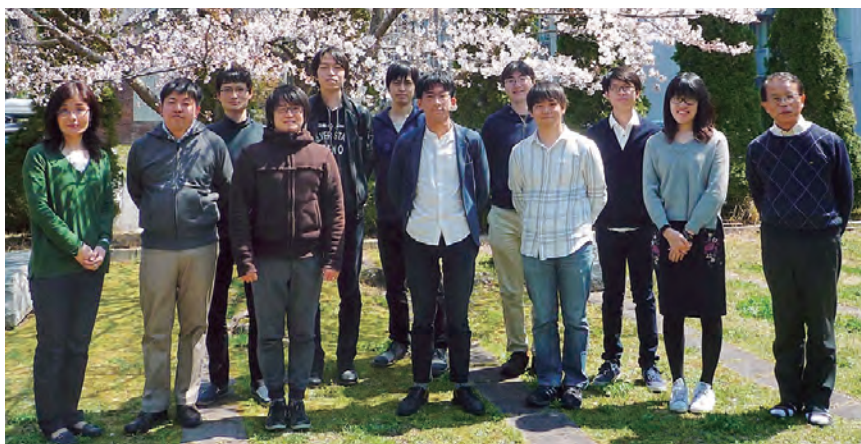
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Scope of Research

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.; Ichihara, N.; Kitano, Y.; Ozawa, F., A Highly Efficient Catalyst for the Synthesis of Alternating Copolymers with Thieno[3,4-*c*]pyrrole-4,6-dione Units via Direct Arylation Polymerization, *Macromolecules*, **47**, 626-631 (2014).

Wakioka, M.; Nakamura, Y.; Montgomery, M.; Ozawa, F., Remarkable Ligand Effect of $P(2\text{-MeOC}_6\text{H}_4)_3$ 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.; 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 (DAP), *Asian J. Org. Chem.*, **7**, 1206-1216 (2018).

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

The combined use of $P(2\text{-MeOC}_6\text{H}_4)_3$ (**L1**) and TMEDA as ligands effectively prevents defect formation in palladium-catalyzed direct arylation polymerization (DAP) 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 PC₇₁BM. In particular, poly(**1b-alt-2**) exhibits the best performance among DAP polymers reported so far (power conversion efficiency (PCE) = 9.0(1)%).

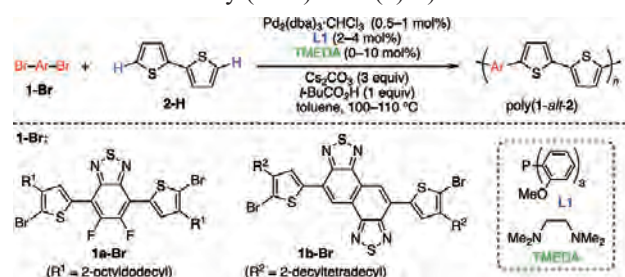


Figure 1. DAP synthesis of DA polymers containing bithiophene units.

Synthesis of π -Conjugated Polymers Containing Benzodithiophene and Benzotriazole Units via Highly Selective Direct Arylation Polymerization (DAP): Effects of Homocoupling Defects on Photovoltaic Performance

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 (DAP). In this study, we applied this catalyst to investigate the effects of homocoupling defects on photovoltaic performance of DA polymers (PBDTBTz) containing benzodithiophene (BDT) and benzotriazole (BTz) units. Specifically, we prepared three types of polymers via DAP and compared their performance in bulk-heterojunction organic solar

cells (OSCs). One is a nearly perfect alternating copolymer, whereas the other two each contain one of the two kinds of homocoupling defects (BDT-BDT or BTz-BTz) (**P1**: $M_n = 31,500$, homocoupling defect < 0.1%; **P2**: $M_n = 22,800$, BDT-BDT defect = 19.3%; **P3**: $M_n = 22,800$, BTz-BTz defect = 18.5%). It was found that BDT-BDT defects significantly deteriorate the OSC performance, whereas BTz-BTz defects little affect the performance. It was also found that PBDTBTz prepared by Migita–Stille cross-coupling polymerization ($M_n = 32,100$) contains a large amount of BTz-BTz defects (13.1%). However, the polymer shows the OSC performance comparable to **P1** (PCE up to 9.9%) because the deterioration due to BTz-BTz defects is small.

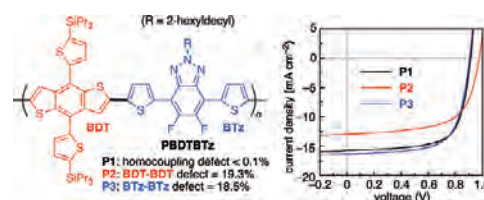


Figure 2. Structure of PBDTBTz and photovoltaic characteristics of PBDTBTz (J - V curves).

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.

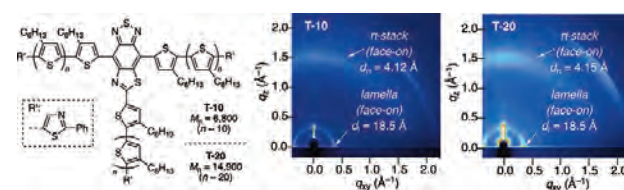


Figure 3. 2D-GIXD patterns of T-shaped π -conjugated polymers (**T-10** and **T-20**) in thin film.