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Controlled Chain-Growth Direct Arylation Polymerization of Asymmetric Push-Pull Aryl Halides

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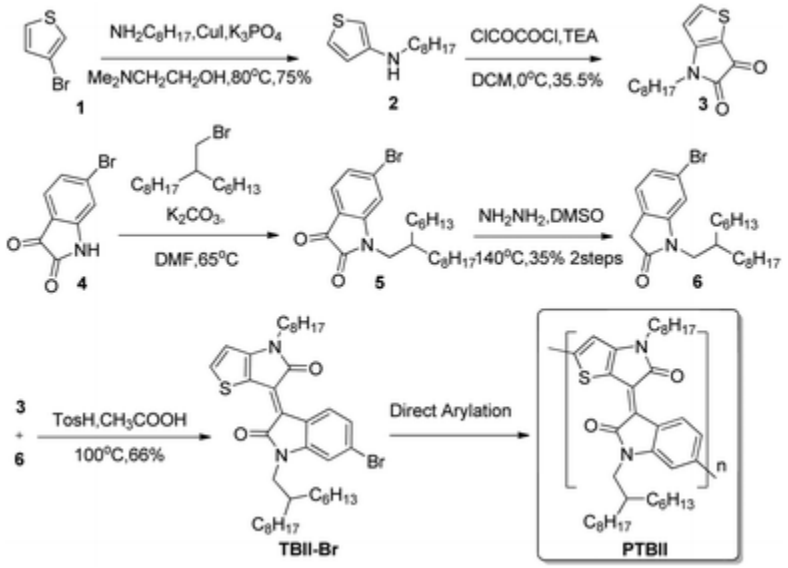
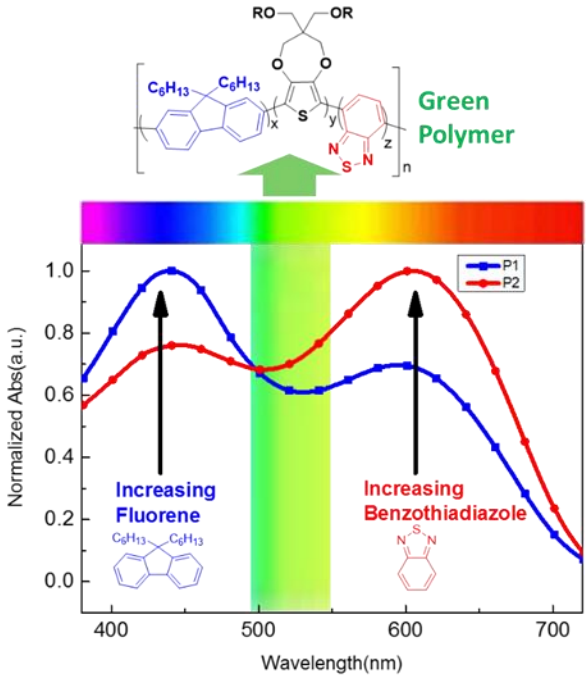
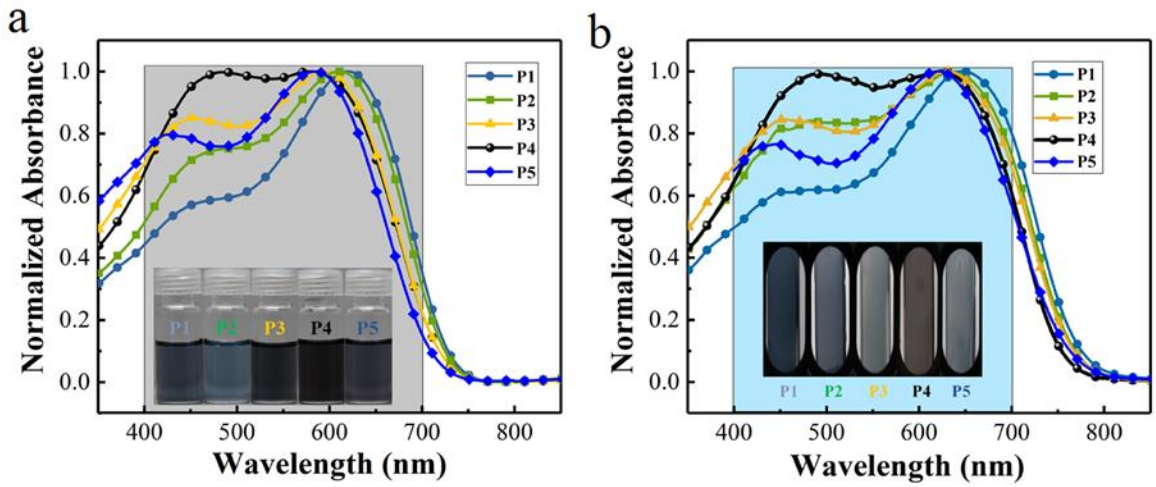
Progress I: Direct arylation polymerization (DArP) has emerged as a greener polymerization method for donor–acceptor (D–A) type conjugated polymers. DArP, in contrast to Stille or Suzuki polymerization, does not involve organometallic compounds as nucleophiles. This feature makes it feasible to directly use asymmetric aryl halides as monomers for preparing D–A polymers. **In this project, we report the design of an asymmetric push–pull thieno-benzo-isoindigo (TBII) based monomer and explore the potential of DArP of TBII, as shown below.** With careful studies on catalytic systems and reaction conditions, we successfully prepared TBII based polymers with high molecular weights. As a control experiment, we also attempted to prepare the symmetric polymer thienoisoindigo-co-isoindigo (PTII-II) via DArP. The result suggested that the use of H-DA-X type monomers is advantageous to achieve high molecular weights in DArP.



Progress II: Electrochromic conjugated polymers (ECPs) have attracted a great deal of attention for their processability, flexibility, and tunable colors through structural design. The potential application of ECPs in displays, smart windows, E-paper, data-storage devices drives the scientific community to create all kinds of conjugated polymers for electrochromic devices. However, most of them present either red or blue in their neutral states, and the green color electrochromic polymers were rarely reported. Using the DArP chemistry we developed, a series of conjugated polymer electrochromes composed of 3,4-propylenedioxythiophene (ProDOT) units, 9,9-dihexyl-9H-fluorene units and the electron-deficient core 2,1,3-benzothiadiazole (BTD) were rationally designed to achieve neutral green colors. We **highlight the random direct arylation polymerization of multi-component monomers to precisely control the absorption spectra of polymer in the visible light region, as illustrated below**. The electrochemical and optical properties, spectroelectrochemical analysis, and electrochromic performance of these green polymers were tested. This straight-forward strategy that can adjust the absorption spectra of ECPs is applicable to other polymer systems with different type of co-monomers.



Progress III: A neutral gray electrochromic conjugated polymer (NG−ECP) was synthesized via direct arylation polymerization by controlling feeding ratios of the monomers. The NG−ECP absorbs across the entire visible region and realizes an obvious color change from gray−black (L* = 49.2, a* = 3.6, b* = −7.7) to transmissive (L* = 85, a* = −4.6, b* = −5.8) with applied a small voltage bias. An optical contrast as high as nearly 70% can be achieved within 10 seconds for the electrochromic (EC) thin films, which is superior to reported gray/black−to−transmissive EC materials. Moreover, long−term cycle stability has been demonstrated with an optical loss as low as 2.1% after 1400 cycles. In addition, a gray black−to−transmissive electrochromic device (ECD) based on the as−prepared EC film was designed using a transparent indium tin oxide (ITO) as the counter electrode for charge storage. The ECD displays high contrasts for 43.6%, switching from a saturated gray black state (L* = 37.8, a* = 2.5, b* = −6.4) to a transmissive state (L* = 72.6, a* = −8.0, b* = −6.5). These outstanding performances potentially make it a promising EC material and can be incorporated into privacy glass, smart windows and other related ECDs.



This project allows the PI to develop direct arylation polymerization chemistry. Currently, the PI is able to scale-up to a kilogram synthesis with our understanding of DArP.