

# Direct arylation polymerization of benzodithiophene with a series of electron acceptors for organic photovoltaic devices

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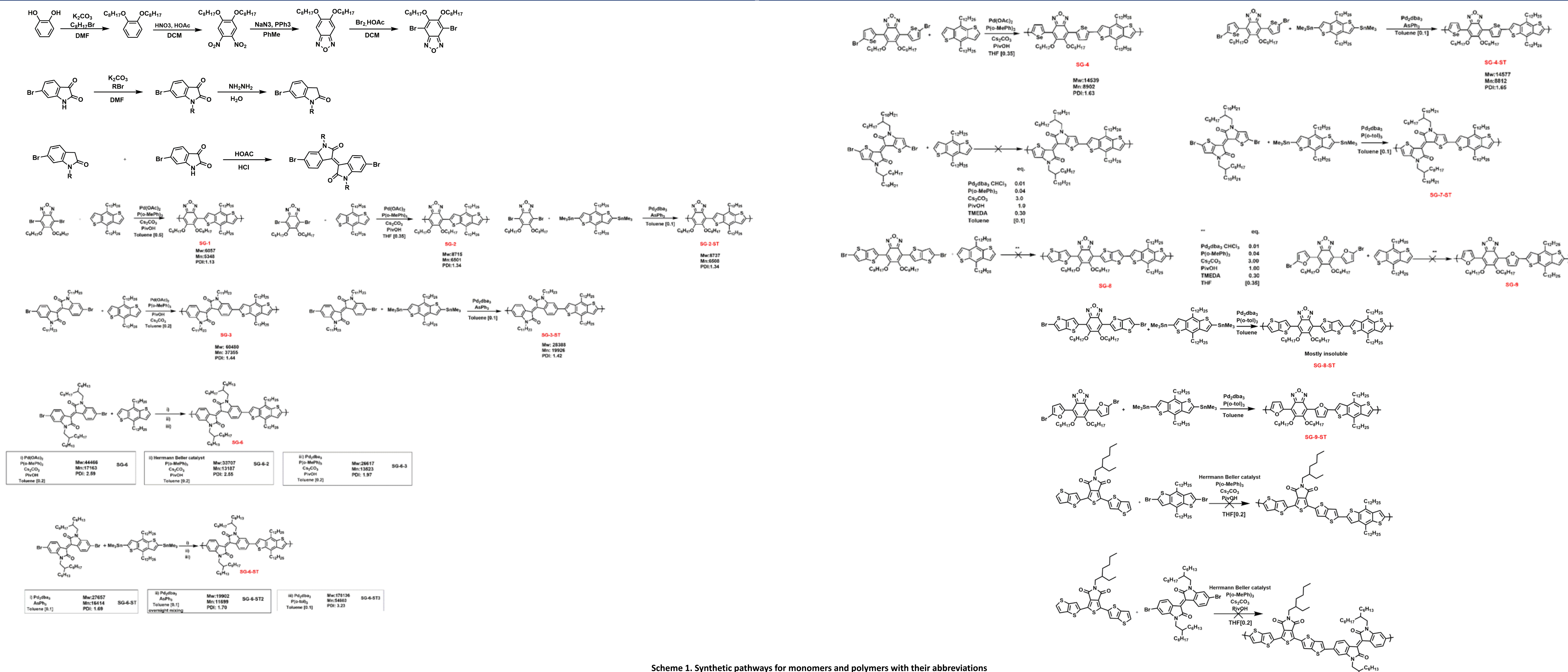
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## 1. Introduction

Conventionally,  $\pi$ -conjugated polymers for optoelectronic applications can be obtained by palladium or nickel catalyzed cross coupling techniques such as Suzuki–Miyaura, Stille, Negishi, and Kumada–Corriu couplings which require several synthetic steps to prepare the metalated monomers and sometimes the synthesis and purification of such compounds is difficult. Direct arylation represents an economically attractive and ecologically benign alternative to the conventional cross-coupling reactions which provides to form carbon-carbon bonds between heteroarenes and aryl halides, which do not require organometallic intermediates thereby significantly reducing both synthetic steps, metallic by-products, and cost. Polymers comprising benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) as the electron donor tend to have promising photovoltaic properties. Its planar conjugated structure, regioregularity, easy modification and high hole mobility makes benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) one of the most successful electron-donor units for synthesis of semiconducting polymers. In this work, benzodithiophene was coupled with a series of different electron acceptors like isoindigo and benzazole to synthesize high molecular weight polymers with minimum structural defects.

## 2. Experimental



## 3. Results and Discussion

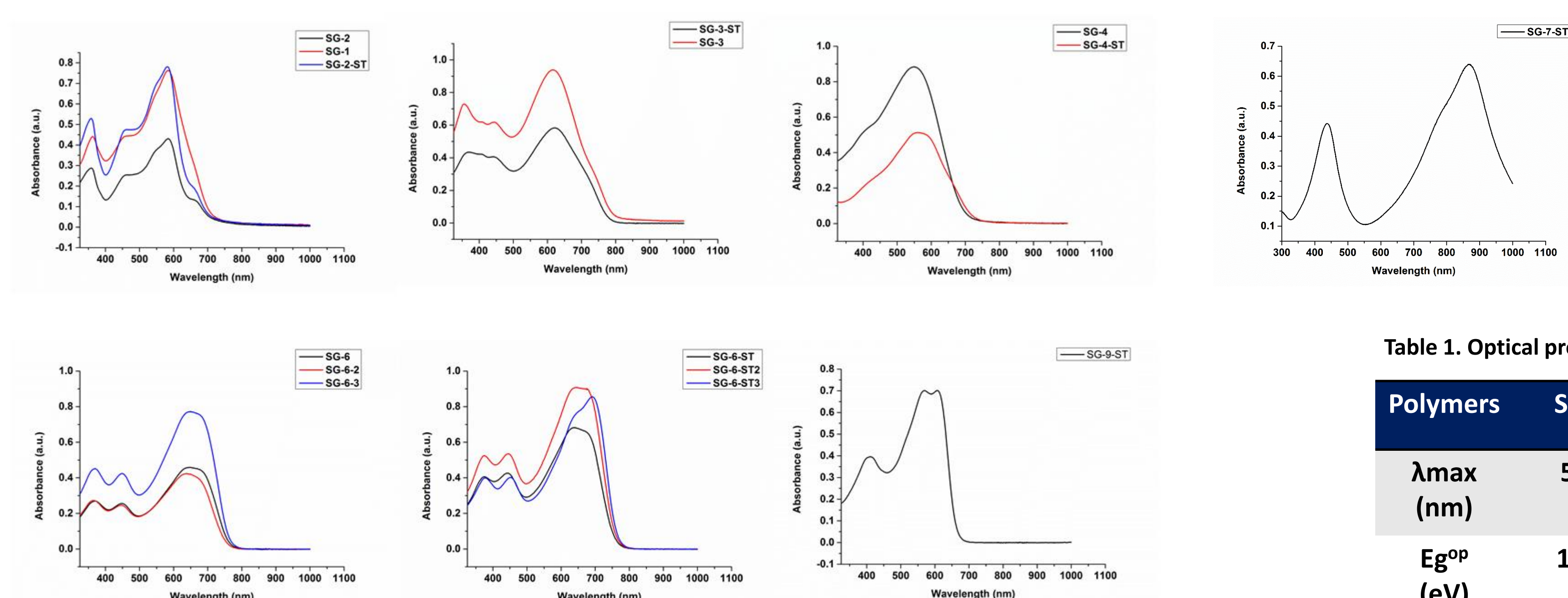


Figure 1. Absorption spectra of polymers

Table 1. Optical properties of polymers

Polymers	SG-1	SG-2	SG-2-ST	SG-3	SG-3-ST	SG-4	SG-4-ST	SG-6	SG-6-2	SG-6-3	SG-6-ST	SG-6-ST2	SG-6-ST3	SG-7-ST	SG-9-ST
$\lambda_{max}$ (nm)	584	582	518	617	620	548	565	654	646	654	652	658	690	867	608
$E_g^{OP}$ (eV)	1.70	1.68	1.71	1.53	1.50	1.69	1.62	1.57	1.60	1.57	1.56	1.58	1.59	1.21	1.82

## 4. Conclusion

Benzodithiophene was cross coupled with a series different electron acceptors comprising benzoxadiazole and isoindigo derivatives via both Stille reaction and direct heteroarylation polymerization (DHAP). To obtain high molecular weight polymers, reaction conditions were optimized with different solvents and catalyst-phosphine-based ligand systems. Polymers synthesized via both methods were compared in terms their absorption spectra and molecular weights. Polymers will be characterized using cyclic voltammetry to determine HOMO and LUMO energy levels and <sup>1</sup>H-NMR for structural defects. For thienothiophene and furan based monomers, polymers cannot be obtained via DHAP probably due to presence of bromine atoms which decrease the energy of activation( $E_a$ ) of the adjacent C–H bonds, allowing undesirable  $\beta$ -defects for some brominated aromatic units. When different C–H bonds are present the lack of selectivity causes branching as well as cross-linking and generally leads to insoluble materials. Ozawa et al. proposed an original strategy called mixed ligand approach. However this methodology did not work in our case. The polymers will be used as active layers for organic solar cells depending on their optoelectronic properties.