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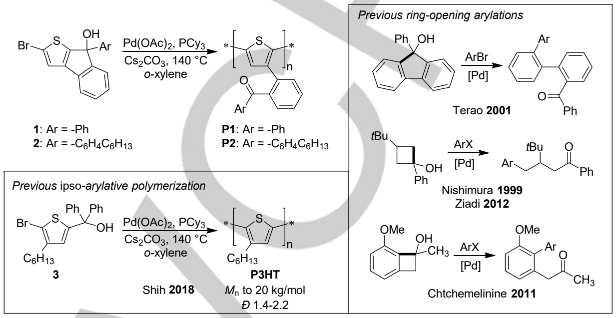
# *ipso*-Arylative Ring-opening Polymerization as a Route to Electron-deficient Conjugated Polymers

Feng-Yang Shih,[a] Deokkyu Choi,[a] Qin Wu,[b] Chang-Yong Nam,[b] Robert. B. Grubbs*,[a]

**Abstract:** *ipso*-Arylative ring-opening polymerization of 2-bromo-8-aryl-8H-indeno[2,1-b]thiophen-8-ol monomers proceeds to $M_n$ up to 9 kg/mol with conversion of the monomer diarylcarbinol groups to pendent conjugated aroylphenyl side chains (2-benzoylphenyl or 2-(4-hexylbenzoyl)phenyl) that influence the optical and electronic properties of the resulting polythiophenes. Poly(3-(2-(4-hexylbenzoyl)phenyl)thiophene) was found to have lower frontier orbital energy levels (HOMO/LUMO = -5.9/-4.0 eV) than poly(3-hexylthiophene) due to the electron-withdrawing ability of the aryl ketone side chains. The electron mobility (~$2\times10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) for poly(3-(2-(4-hexylbenzoyl)phenyl)thiophene) was found to be significantly higher than the hole mobility (~$8\times10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$), which suggests such polymers are candidates for n-type organic semiconductors. Density functional theory calculations suggest that backbone distortion resulting from side-chain steric interactions could be a key factor influencing charge mobilities.

Ring-opening polymerization (ROP) is a powerful method for the preparation of functionalized polymers. The majority of ROP methods use heterocyclic monomers (ethers,[1] lactones,[2] lactams,[3] oxazolines[4]) and ionic polymerization methods,[5] with a few important exceptions, including radical ring-opening polymerization,[6] ring-opening metathesis polymerization,[7] and other metal-catalyzed ROP processes involving allyl-Pd complexes or Pt-catalyzed opening of silaferrocenophanes.[8]

While Pd-catalyzed aryl-aryl coupling reactions, particularly Stille and Suzuki-Miyaura reactions,[9] have been widely used for the preparation of conjugated polymers, these methods are not easily converted to ring-opening methods. *ipso*-Arylative coupling methods[10] that involve diaryl[11] or dialkylcarbinol[12] leaving groups generate ketone by-products that, with appropriate monomer design, can remain bound to the polymer backbone. With a conjugated polymer backbone, this strategy has the benefit of enabling the electron-withdrawing ketone moiety to directly influence the electronic properties of the polymer. While several examples of ring-opening arylative cross-coupling reactions have been reported with small molecules, including the *ipso*-arylation of 9-phenylfluoren-9-ol with phenyl bromide,[10b] as well as ring-opening arylations of cyclobutanols[13] and norbornenols,[14] there are no reports of polymerization by these methods (Scheme 1).



**Scheme 1.** Asterisks indicate end-group variability. References: Shih 2018,[15] Terao 2001,[10b] Nishimura 1999,[13a] Ziadi 2012,[13b] Chtchemelinine 2011.[13c]

In a previous study, we investigated the *ipso*-arylative cross-coupling polymerization of 5-bromo-4-hexylthiophen-2-yl)diphenylmethanol (**3**) to prepare poly(3-hexylthiophene) (P3HT) (Scheme 1).[15] While P3HT with $M_n$ values of up to 20 kg/mol could be prepared, molecular weights were ultimately limited by end group loss over the course of the polymerization and dispersity values were typical of a step growth polymerization (*Đ* 1.4-2.2).[15] An additional limitation, common to all *ipso*-arylation reactions, was the generation of one equivalent of ketone (benzophenone) for each monomer coupling step.

To side-step this latter problem and, in the process, examine the effect of electron-withdrawing aroylphenyl side chains on the optical and electronic properties of the polythiophene backbone, we have designed two monomers, 2-bromo-8-phenyl-8H-indeno[2,1-b]thiophen-8-ol (**1**) and 2-bromo-8-(4-hexylphenyl)-8H-indeno[2,1-b]thiophen-8-ol (**2**), capable of undergoing *ipso*-arylative ring-opening cross-coupling polymerization to result in polymers **P1** and **P2** in which the aroylphenyl group that results from carbinol extrusion is retained as an electron-withdrawing moiety conjugated to the polythiophene backbone (Scheme 1).

ROP of monomer **1** was carried out by *ipso*-arylative cross-coupling under conditions that were previously found to be effective for the polymerization of 5-bromo-4-hexylthiophen-2-yl)diphenylmethanol (Scheme 1).[15] Monomer **1** (0.1 M) was heated with Pd(OAc)$_2$ (3 mM), PCy$_3$ (6 mM), and Cs$_2$CO$_3$ (0.15 M) in *o*-xylene at 140 °C for 48 h. Over the course of the polymerization, formation of an insoluble red powder was observed. After sequential washing of the isolated solid with acetone and THF, the fraction of **P1** that was isolated by Soxhlet extraction with CHCl$_3$ was partially dissolved in THF, and found by SEC to have a moderate molecular weight ($M_n$ = 10 kg/mol vs PS standards) and a dispersity typical of a step-growth polymerization (*Đ* = 2.0). The relatively low yield (49% for the CHCl$_3$ fraction) and formation of insoluble material suggest that the polymerization proceeds to a higher molecular weight than is

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**Table 1.** Polymerization conditions and characterization data for polymers **P2**.[a]

| | Monomer (conc., M) | [Pd(OAc)$_2$] (mM) | t (h) | T (°C) | $M_n$ [b] (kg/ mol) | Đ [b] | Yield (%)[c] |
|---|---|---|---|---|---|---|---|
| **P2a** | **2** (0.5) | 3 | 48 | 140 | 9.0 | 2.0 | 76 |
| **P2b** | **2** (0.5) | 5 | 48 | 140 | 4.9 | 1.8 | 67 |
| **P2c** | **2** (0.1) | 5 | 72 | 170 | 7.0 | 1.6 | 58 |

[a] [**1**] = 0.1 M or [**2**] = 0.1 or 0.5 M, [Pd(OAc)$_2$] = 3 or 5 mM, [PCy$_3$] = [Pd(OAc)$_2$] × 2, and Cs$_2$CO$_3$ (0.15 M) heated in *o*-xylene at 140 or 170 °C for 48-72 h; [b] number-average molecular weight ($M_n$) and dispersity (Đ) of polymers in chloroform fractions were estimated by SEC in THF with polystyrene standards; [c] yield of the CHCl$_3$ fraction based on 100% conversion.

apparent by SEC, but further characterization and thin-film processing of **P1** was difficult because of the poor solubility.

To increase solubility, polymerization of monomer **2**, an analog of monomer **1** with an *n*-hexyl side-chain in the *para*-position of the phenyl group, was investigated under similar conditions and found to proceed without precipitation to afford **P2** as a red powder after Soxhlet purification (washing with acetone followed by isolation with CHCl$_3$) with a high yield of the CHCl$_3$-soluble fraction (76%, Table 1). **P2** showed significantly higher solubility in THF, CHCl$_3$, and *o*-dichlorobenzene than **P1**. **P2a**, prepared with a 3 mM concentration of Pd(OAc)$_2$, showed a comparable molecular weight ($M_n$ = 9.0 kg/mol vs PS standards) and dispersity (Đ = 2.0) to **P1** by SEC (Table 1). Higher catalyst loading (5 mM) resulted in a lower molecular weight (**P2b**, $M_n$ = 4.9 kg/mol) and a lower yield (67%) (Table 1), which suggests that the catalyst is playing a role in the loss of active end-groups, as has been observed previously for *ipso*-arylative polymerization of monomer **3**.[15] Higher temperature (170 °C) with lower [**2**] (0.1 M) resulted in slightly lower molecular weight (**P2c**, $M_n$ = 7 kg/mol) and lower yield (58%) than **P2a**, suggesting the occurrence of catalyst decomposition or other side reactions.

The higher solubility of polymer **P2** allowed characterization by $^1$H NMR. In CD$_2$Cl$_2$, peaks corresponding to the arylene (7.0-7.5 ppm), thienyl (6.51 ppm), and *n*-hexyl side chains (2.6, 1.5, 1.3, and 0.87 ppm) were observed (Figure S1). IR spectra showed a peak at 1660 cm$^{-1}$ for both **P1** and **P2a** corresponding to side-chain carbonyl groups and, for **P2a**, a peak at 2800-3000 cm$^{-1}$ corresponding to alkyl C-H stretching vibrations in the *n*-hexyl groups (Figure S2).

MALDI-TOF MS analysis showed both **P1** and **P2** to have a primary series of peaks with a mass difference between peaks that corresponds to the mass of the repeating units (262.3 g/mol for **P1** and 346.5 g/mol for **P2**) and *m/z* values suggesting chains lacking a terminal bromide (Figure S4), as a result of either protodehalogenation or reductive coupling of thienyl halide chain ends (Figure S5), as has previously been observed for the *ipso*-arylative polymerization of monomer **3**. Both **P1** and **P2** also show minor series of peaks assigned to cationization through loss of hydroxide and transfer of phenyl/4-hexylphenyl groups to chain ends (Figure S4-S5).

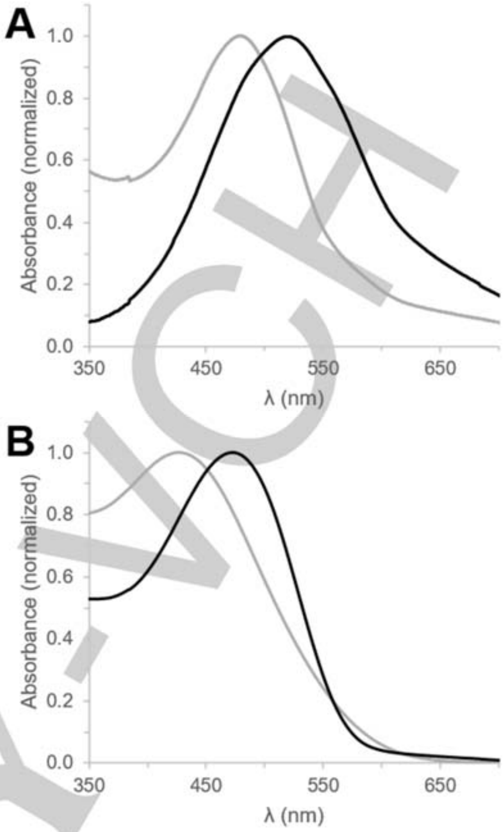

**Figure 1.** UV-Vis absorbance spectra of (A) **P1** in CHCl$_3$ (0.02 mg/mL) (gray) and thin film (cast on glass from 0.5 mg/mL CHCl$_3$ solution) (black), and (B) **P2a** in solution (gray) and thin film (black).

Absorbance spectra for **P1** and **P2a** were acquired in solution (0.02 mg/ml, CHCl$_3$) and in thin films (glass, 0.5 mg/ml CHCl$_3$ solution) (Figure 1). For both **P1** and **P2a**, $\lambda_{max}$ in thin films shifted to the red from $\lambda_{max}$ in solution (0.24 eV, from 480 to 530 nm, for **P1**; 0.30 eV, from 430 to 480 nm, for **P2a**) as a result of increased intermolecular interactions in the thin film (Figure 1). The thin-film optical band gaps were estimated as 2.01 eV for **P1** ($\lambda_{onset}$ = 620 nm) and 2.17 eV for **P2a** ($\lambda_{onset}$ = 570 nm).

Electrochemical band gaps for **P1** (2.09 eV; $E_{ox.\ onset}$ = 0.58 V; $E_{red.\ onset}$ = -1.25 V) and **P2** (2.18 eV; $E_{ox.\ onset}$ = 0.82 V; $E_{red.\ onset}$ = -1.08 V) measured by cyclic voltammetry were found to be in good agreement with the optical band gaps (Figure 2). The larger bandgap for **P2a** may result from backbone distortion induced by the hexyl side-chains.[16] The aroylphenyl side-chains lead to significantly lower frontier molecular orbital (FMO) energy levels for **P1** (HOMO = -5.68 eV and LUMO = -3.85 eV) and **P2a** (HOMO = -5.92 eV and LUMO = -4.02 eV) as compared to those which have been reported for P3HT (HOMO = -4.75 eV and LUMO = -2.83 eV) (Table 2).[17]

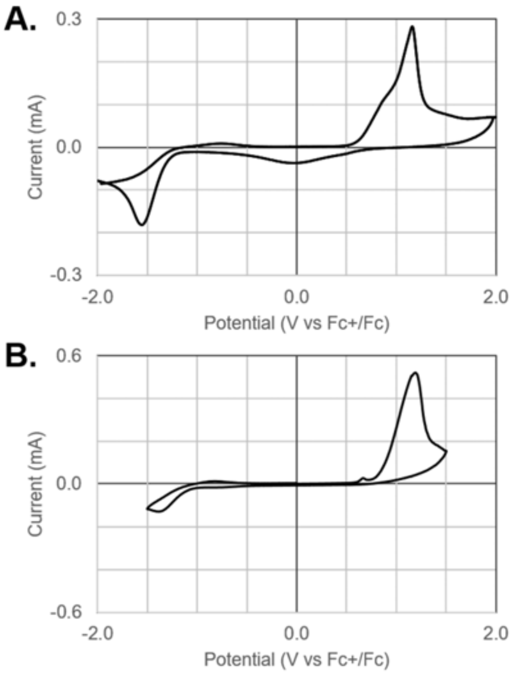

**Figure 2.** Cyclic voltammograms of (A) **P1** and (B) **P2a** in $Bu_4NOH$ (0.1 M)/$CH_3CN$. Polymer in $CHCl_3$ (1 mg/ml) were drop-cast on a carbon glass working electrode .Conducting electrode: Au wire; Reference electrode: Pt wire in $AgNO_3$ (0.01 M)/$Bu_4NOH$ (0.1 M)/ $CH_3CN$.

**Table 2.** Optical and electronic properties of **P1** and **P2a**

| | $\lambda_{onset}$ (nm) [a] | HOMO/ LUMO (eV) [b] | $E_{g,opt}$ (eV)[c] | $E_{g,elec}$ (eV) [d] | $\mu_h$[e] (cm$^2$ V$^{-1}$ s$^{-1}$) | $\mu_e$[f] (cm$^2$ V$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|---|
| **P1** | 618 | -5.68/ -3.85 | 2.01 | 2.09 | 7.9 (± 2.0) × $10^{-7}$ | Not measured |
| **P2a** | 571 | -5.92/ -4.02 | 2.17 | 2.18 | 7.8 (± 1.3) × $10^{-6}$ | 2 (± 1.6) × $10^{-3}$ |

[a] Onset wavelength of absorbance in spectrum; [b] HOMO = -(5.1 + $E_{\text{oxidation onset}}$) eV; LUMO = -(5.1 + $E_{\text{reduction onset}}$) eV; [c] Optical bandgap $E_{g,opt}$ = 1240 eV·nm/$\lambda_{onset}$; [d] Electrochemical bandgap $E_{g,elec}$= -(LUMO-HOMO); [e] Hole mobility ($\mu_h$) averaged over 8 measurements with standard deviation in parentheses calculated from SCLC model. [f] Electron mobility ($\mu_e$) averaged over 6 measurements with standard deviation in parentheses calculated from SCLC model.

Hole mobilities ($\mu_h$) for each polymer were measured by analyzing current density-voltage ($J$–$V$) characteristics of hole-only ohmic devices with the space-charge-limited current (SCLC) model.[18] For hole mobility measurements, SCLC devices were built in an ITO/$MoO_x$/polymer/$MoO_x$/Au architecture (Figure S6).[19] **P1** showed a hole mobility ($\mu_h$) of 8 × $10^{-7}$ cm$^2$ V$^{-1}$ s$^{-1}$ (Figure S8), while $\mu_h$ for **P2a** was found to be an order of magnitude higher (8 × $10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$), though still two orders of magnitude lower than $\mu_h$ values reported for P3HT (1.1 × $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for $M_n$ = 9.7 kg/mol).[20] In comparing **P1** and **P2**, the higher hole mobility observed for **P2** likely results from its higher solubility, which results in films with more effective interchain π-stacking consistent with the larger red shift observed in the absorbance spectrum of **P2a** compared with **P1** (Figure 1).[21]

The low LUMO energy of **P2** suggested it could also serve as an *n*-type semiconducting polymer. The electron mobility ($\mu_e$) of **P2a** was measured in devices with an FTO/$TiO_2$/Polymer/Al architecture, in which $TiO_2$ was used as ohmic contact (Figure S7).[22] The $\mu_e$ for **P2a** calculated using the SCLC model was ~2×$10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, which is significantly higher than $\mu_e$ values reported for P3HT (~2.1×$10^{-9}$ cm$^2$ V$^{-1}$ s$^{-1}$),[23] and comparable to $\mu_e$ values reported for organic non-fullerene molecules and polymers used as acceptors in OPV devices with high efficiencies (PCE from 6-11% for $\mu_e$ from 1-3 ×$10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$).[24]

Density functional theory (DFT) calculations (B3LYP/6-31G(d)) were carried out on a model **P1** octamer to confirm the effect of the aroylphenyl side chains on the observed properties of **P1** and **P2**. The S-C-C-S dihedral angles between neighboring thienyl units were examined and compared to those in P3HT calculated at the same level.[25] In **P1**, these angles were found to range from 133-142°, vs 142-160° in P3HT and 180° in a perfectly *trans*-planar structure. Thus the 2-benzoylphenyl side chains in **P1** appear to decrease planarity of the polythiophene backbone and reduce the conjugation length of the polymer, which would be consistent with the lower $\mu_h$ measured for **P1** as compared to P3HT. With time-dependent DFT and a polarizable continuum model of the chloroform solvent, the lowest singlet excitation of the **P1** octamer model was calculated to be 2.50 eV (495 nm) with a large oscillator strength (1.5849), which is in good agreement with the experimental $\lambda_{max}$ measured for **P1** (~500 nm) in chloroform (Figure 1a). The calculated natural transition orbitals (NTO)[26] that are used to approximate the hole (*i.e.*, HOMO) and electron (*i.e.*, LUMO) of this excitation show that, while the hole is essentially confined to the backbone, the electron is delocalized to the side-chain aromatic rings (Figure 3). Such delocalization would enhance inter-chain interactions due to increased orbital overlap and reduce trapping of electrons on a single chain, which supports the higher electron mobility measured experimentally.

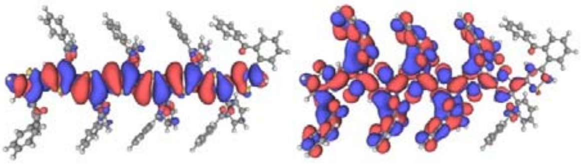

**Figure 3.** Natural transition orbitals that represent the hole (left) and electron (right) of the lowest singlet transition in a model **P1** octamer.

These results show that *ipso*-arylative ring-opening polymerization of 2-bromo-8-aryl-8H-indeno[2,1-b]thiophen-8-ol monomers **1** and **2** can proceed with retention of organic leaving groups that can significantly influence polymer electronic and optical properties. While the side reactions typical of *ipso*-arylative polymerization conditions identified to date and the steric factors introduced by the monomer structural requirements appear to be limiting factors, polymer **P2** has electron mobility values and frontier MO energy levels comparable to other *n*-type non-fullerene acceptor materials that have been used in high-performance OPV devices. Further optimization of the synthesis of conjugated polymers bearing diarylketone substituents by *ipso*-

arylation or other methods could enable the identification of new *n*-type organic semiconductors for a range of electronic applications.

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**Keywords:** conducting materials • cross-coupling • *ipso*-arylative polymerization • palladium • ring-opening polymerization

[1] A. Sunder, R. Hanselmann, H. Frey, R. Mülhaupt, *Macromolecules* **1999**, *32*, 4240-4246.
[2] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147-6176.
[3] H. Hall Jr, *J. Am. Chem. Soc.* **1958**, *80*, 6404-6409.
[4] S. Kobayashi, T. Tokuzawa, T. Saegusa, *Macromolecules* **1982**, *15*, 707-710.
[5] J. V. Crivello, J. Lam, *Macromolecules* **1977**, *10*, 1307-1315.
[6] a) W. J. Bailey, Z. Ni, S. R. Wu, *Macromolecules* **1982**, *15*, 711-714; b) A. D. Asandei, I. W. Moran, *J. Am. Chem. Soc.* **2004**, *126*, 15932-15933.
[7] a) C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.* **2007**, *32*, 1-29; b) R. B. Grubbs, R. H. Grubbs, *Macromolecules* **2017**, *50*, 6979-6997.
[8] a) M. Suzuki, A. Ii, T. Saegusa, *Macromolecules* **1992**, *25*, 7071-7072; b) S. Kim, D. Takeuchi, K. Osakada, *J. Am. Chem. Soc.* **2002**, *124*, 762-763.
[9] a) M. Jayakannan, J. L. J. van Dongen, R. A. J. Janssen, *Macromolecules* **2001**, *34*, 5386-5393; b) Y. S. Park, T. S. Kale, C. Y. Nam, D. Choi, R. B. Grubbs, *Chem. Commun.* **2014**, *50*, 7964-7967; c) Y. S. Park, Q. Wu, C. Y. Nam, R. B. Grubbs, *Angew. Chem. Int. Ed.* **2014**, *53*, 10691-10695.
[10] a) Y. Terao, H. Wakui, M. Nomoto, T. Satoh, M. Miura, M. Nomura, *J. Org. Chem.* **2003**, *68*, 5236-5243; b) Y. Terao, H. Wakui, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2001**, *123*, 10407-10408.
[11] a) S. M. Bonesi, M. Fagnoni, A. Albini, *Angew. Chem. Int. Ed.* **2008**, *47*, 10022-10025; b) J. R. Bour, J. C. Green, V. J. Winton, J. B. Johnson, *J. Org. Chem.* **2013**, *78*, 1665-1669.
[12] a) S. M. Bonesi, M. Fagnoni, *Chem. Eur. J.* **2010**, *16*, 13572-13589; b) M. Iwasaki, Y. Araki, S. Iino, Y. Nishihara, *J. Org. Chem.* **2015**, *80*, 9247-9263.
[13] a) T. Nishimura, S. Uemura, *J. Am. Chem. Soc.* **1999**, *121*, 11010-11011; b) A. Ziadi, R. Martin, *Org. Lett.* **2012**, *14*, 1266-1269; c) A. Chtchemelinine, D. Rosa, A. Orellana, *J. Org. Chem.* **2011**, *76*, 9157-9162.
[14] Y. Li, W. Yang, G. Cheng, D. Yang, *J. Org. Chem.* **2016**, *81*, 4744-4750.
[15] F.-Y. Shih, S. Tian, N. Gallagher, Y. S. Park, R. B. B. Grubbs, *Polym. Chem.* **2018**, *9*, 3223-3231.
[16] B. Friedel, C. R. McNeill, N. C. Greenham, *Chem. Mater.* **2010**, *22*, 3389-3398.
[17] C. J. Shi, Y. Yao, Y. Yang, Q. B. Pei, *J. Am. Chem. Soc.* **2006**, *128*, 8980-8986.
[18] C. Y. Nam, *J. Phys. Chem. C* **2012**, *116*, 23951-23956.
[19] A. Buckley, D. Pickup, C. Yates, Y. Zhao, D. Lidzey, *J. Appl. Phys.* **2011**, *109*, 084509.
[20] C. Goh, R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. M. Fréchet, *Appl. Phys. Lett.* **2005**, *86*, 122110.
[21] J. Mei, Z. Bao, *Chem. Mater.* **2014**, *26*, 604-615.
[22] S. Sandén, O. Sandberg, Q. Xu, J.-H. Smått, G. Juška, M. Lindén, R. Österbacka, *PCCP* **2012**, *14*, 14186-14189.
[23] M. Ahmed, I. Hummelgen, *Int. J. Electroactive Mater.* **2013**, *1*, 60-63.
[24] C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder, X. Zhan, *Nat. Rev. Mater.* **2018**, *3*, 18003.
[25] M. J. Frisch, Wallingford, CT, **2016**.
[26] R. L. Martin, *The Journal of Chemical Physics* **2003**, *118*, 4775-4777.

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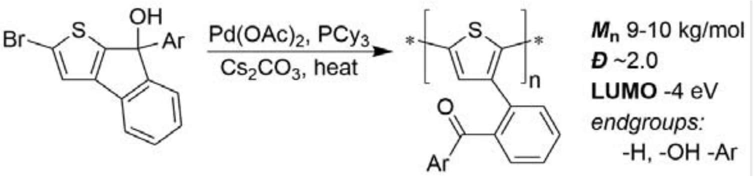
Layout 1:

## COMMUNICATION



**Dangling modifiers.** *ipso*-Arylative cross-coupling polymerization leads to *n*-type polythiophenes with pendent electron-withdrawing diarylketone groups.

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