Supplemental Information

Exploration and development of gold- and silver-catalyzed cross
dehydrogenative coupling toward donor-acceptor π-conjugated polymer
synthesis

Lauren J. Kang, a Liwen Xing, b and Christine K. Luscombe c

aDepartment of Chemistry, University of Washington, Seattle, WA 98195
bMolecular Engineering and Sciences Institute, University of Washington, Seattle, WA 98195
Department of Material Science & Engineering, University of Washington, Seattle, WA 98195

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General Procedures

All manipulation of air- and/or moisture-sensitive compounds were carried out using standard Schlenk and glovebox techniques under a dry nitrogen atmosphere. Anhydrous 1,4-dioxane, chloro(triphenylphosphine)gold(I), deuterium oxide, 3,3’-dihexyl-2,2’-bithiophene, gold(III) chloride, 2-methylene thiophene, 4-nitrotoluene, 2,2’,3,3’,5,5’,6,6’-octafluorobiphenyl, pentafluorobenzene, pivalic acid, sodium trimethylacetate hydrate, and 1,2,4,5-tetrafluorobenzene were used as purchased. Pivaloyloxy-1,2-benziodoxol-3(1H)-one (PBX),[1] silver pivalate (AgOPiv),[2] and acetate(triphenylphosphine)gold(I) (PPh3AuOAc)[3] were synthesized using previously reported methods. 1H NMR and 2H NMR spectra were collected on a Bruker AV 500 spectrometer operating at 500 MHz. For 1H NMR, deuterated chloroform was used. MALDI-TOF measurements were run on a Bruker Autoflex II instrument using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile as a matrix. Dispersity values were measured using a Waters Breeze GPC system in chloroform with 0.1 % triethylamine by volume, against a polyethylene glycol/oxide (PEG/PEO) standard, at a flowrate of 1 mg/ml at 30 °C.

Representative 1H NMR spectrum from small molecule studies

![1H NMR spectrum](image)

**Figure S1** Representative 1H NMR spectrum of small molecule coupling studies showing the aromatic region.
Spectral Data of Polymers

MALDI data

![Figure S2 Polymer A.](image)

Table S1 Notable M/Z values observed from MALDI of Polymer A. \( m \) and \( n \) were calculated using the known MW values of each monomer species.

<table>
<thead>
<tr>
<th>M/Z</th>
<th>( m )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3254</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>3402</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>3476</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>3587</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>3735</td>
<td>9</td>
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<td>3920</td>
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<td>4</td>
</tr>
<tr>
<td>4068</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>
Table S2 Notable M/Z values observed from MALDI of Polymer B. m and n were calculated using the known MW values of each monomer species.

<table>
<thead>
<tr>
<th>M/Z</th>
<th>m</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>3181</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>3218</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>3514</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>3811</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>3847</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>4144</td>
<td>8</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure S4 Example MALDI spectrum of Polymer B.
**NMR spectra**

**Figure S5** Example $^1$H NMR (500 MHz, CDCl$_3$) of Polymer B at 168 h time point.

**Figure S6** Example $^{19}$F NMR (470 MHz, CDCl$_3$) of Polymer B. The presence of multiple peaks supports that the polymer is not a perfectly alternating polymer.
Calculating % Alt, $M_n$, and DP Using $^1$H NMR

% Alt, $M_n$, and DP were calculated using the integration of end groups ($I_a$, $I_b$, $I_a'$, and $I_b'$) and aromatic protons ($I_h$ and $I_c$) on the chain backbone.

**Equation S1.** DP calculation, using end-group analysis.

$$\text{DP} = \frac{2I_c}{I_a + I_b'} + \frac{I_h}{I_a + I_b'}$$

Note that $I_a = I_b$ and $I_a' = I_b'$ and $I_a, I_b'$ were chosen because they appear as clean non-overlapping doublets in the NMR spectra.

**Equation S2.** $M_n$ calculation, using end-group analysis.

$$M_n = \frac{I_c}{I_a + I_b'} (MW_D + MW_A) + \frac{I_h}{I_a + I_b'} MW_D + MW_D$$

**Equation S3.** % Alt calculation.

$$% \text{alt} = \frac{I_c}{I_c + I_h} * 100\%$$

**Table S3** $M_n$ and DP of Polymers A and B at different time points during polymerization.

<table>
<thead>
<tr>
<th>Timepoint (h)</th>
<th>$M_n$ of Polymer A (kg/mol)</th>
<th>DP of Polymer A</th>
<th>$M_n$ of Polymer B (kg/mol)</th>
<th>DP of Polymer B</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>4.1</td>
<td>15</td>
<td>5.6</td>
<td>17</td>
</tr>
<tr>
<td>48</td>
<td>4.8</td>
<td>18</td>
<td>6.7</td>
<td>20</td>
</tr>
<tr>
<td>96</td>
<td>4.8</td>
<td>18</td>
<td>7.5</td>
<td>22</td>
</tr>
<tr>
<td>120</td>
<td>4.9</td>
<td>18</td>
<td>7.9</td>
<td>24</td>
</tr>
<tr>
<td>144</td>
<td>4.9</td>
<td>18</td>
<td>8.7</td>
<td>26</td>
</tr>
<tr>
<td>168</td>
<td>4.5</td>
<td>16</td>
<td>8.1</td>
<td>25</td>
</tr>
<tr>
<td>192</td>
<td>5.1</td>
<td>18</td>
<td>9.4</td>
<td>28</td>
</tr>
</tbody>
</table>
Calculation of Deuterium Incorporation (%)

Deuterium incorporation was calculated using $^2$H NMR integration of the deuterated arene signal ($I_P$) against the signal of internal standard, 10 µL deuterated DMSO (0.141 mmol) ($I_D$).

**Equation S4.** Deuterium incorporation calculation.

\[
\text{Deuterium incorporation} \% = \frac{I_P}{I_D} \times \frac{0.141 \text{ mmol} \times 6}{0.1 \text{ mmol}} \times 100 \%
\]
$^1$H NMR for Synthesis of PPh$_3$Au(I)-C$_6$F$_5$ with and without Sodium tert-Butoxide (NaO'Bu)

The complex PPh$_3$Au(I)-C$_6$F$_5$ could not be formed in the absence of a base, such as NaO'Bu, even when one equivalent of NaOPiv was added. The $^1$H NMR of PPh$_3$Au(I)-C$_6$F$_5$ has been reported previously.\textsuperscript{[4]}

**Control Experiment of Homo-coupling of 2-Methylthiophene**

\[
\begin{align*}
\text{2-Methylthiophene} & \quad \text{AgOPiv (0.35 eq.)} \\
& \quad \text{PPh$_3$AuOAc (5 mol %)} \\
& \quad \text{PBX (1.5 eq.)} \\
& \quad \text{4-nitrotoluene (int. std.)} \\
& \quad 1,4\text{-dioxane, 20 h, 110 °C} \\
\rightarrow & \quad \text{Homo-coupled product}
\end{align*}
\]

Scheme S1 Control experiment to observe homo-coupling of 2-methylthiophene.

When the 2-methylthiophene species was reacted without pentafluorobenzene, 21 ± 8 % yield of the homo-coupled product was formed when run in triplicate.
$^1$H NMR for the Reaction Shown in Scheme 7

![Chemical structures and NMR spectrum](image)

**Figure S9** $^1$H NMR spectrum of the reaction shown in Scheme 7 of the aromatic region.

**References**


