

Supplemental Information

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

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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-methylthiophene, 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

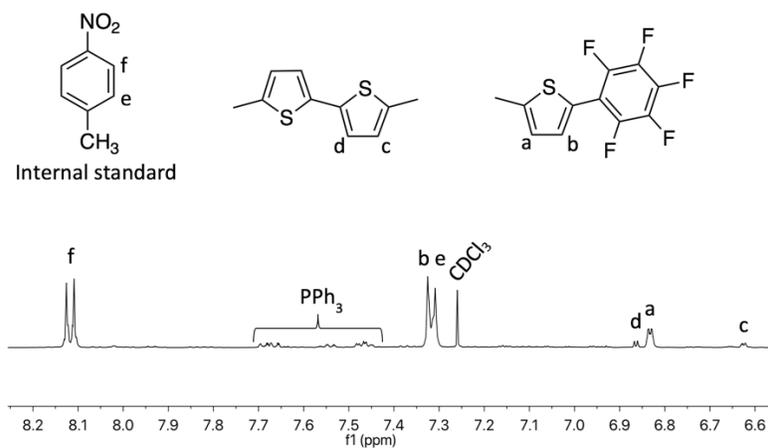


Figure S1 Representative ¹H NMR spectrum of small molecule coupling studies showing the aromatic region.

Spectral Data of Polymers

MALDI data

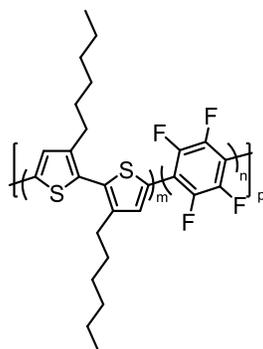


Figure S2 Polymer A.

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.

<i>M/Z</i>	<i>m</i>	<i>n</i>
3254	8	4
3402	8	5
3476	10	1
3587	9	4
3735	9	5
3920	10	4
4068	10	5

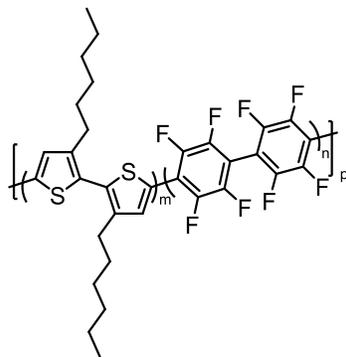


Figure S3 Polymer B.

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.

M/Z	m	n
3181	6	4
3218	7	3
3514	7	4
3811	7	5
3847	8	4
4144	8	5

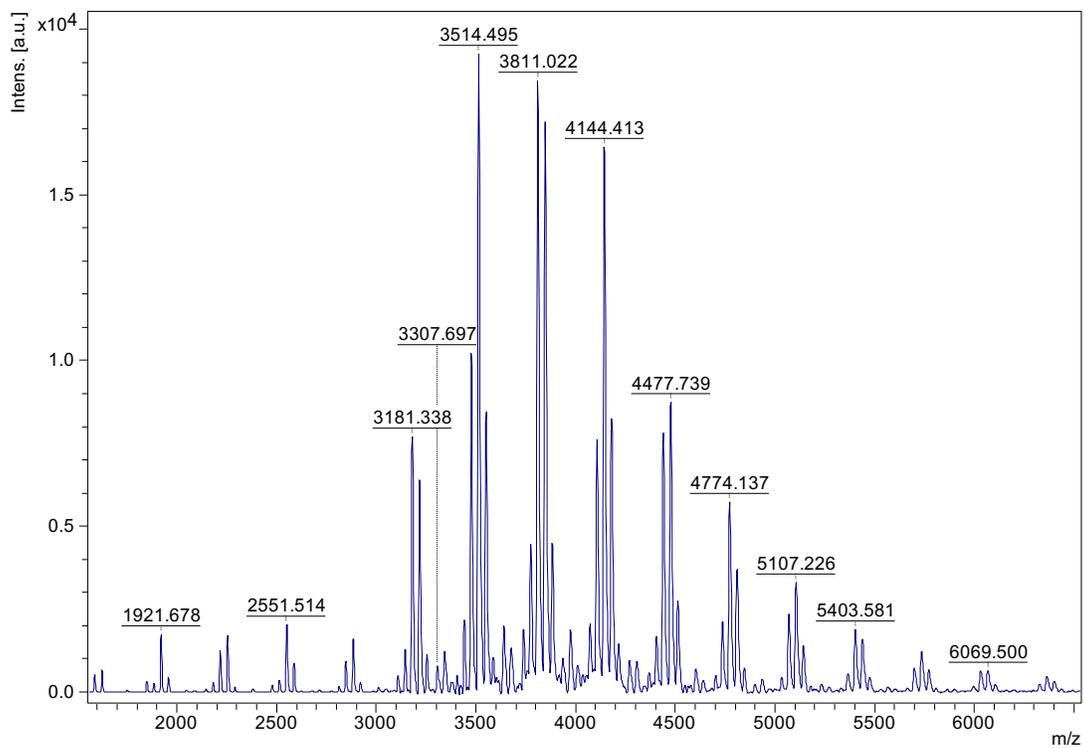


Figure S4 Example MALDI spectrum of Polymer B.

NMR spectra

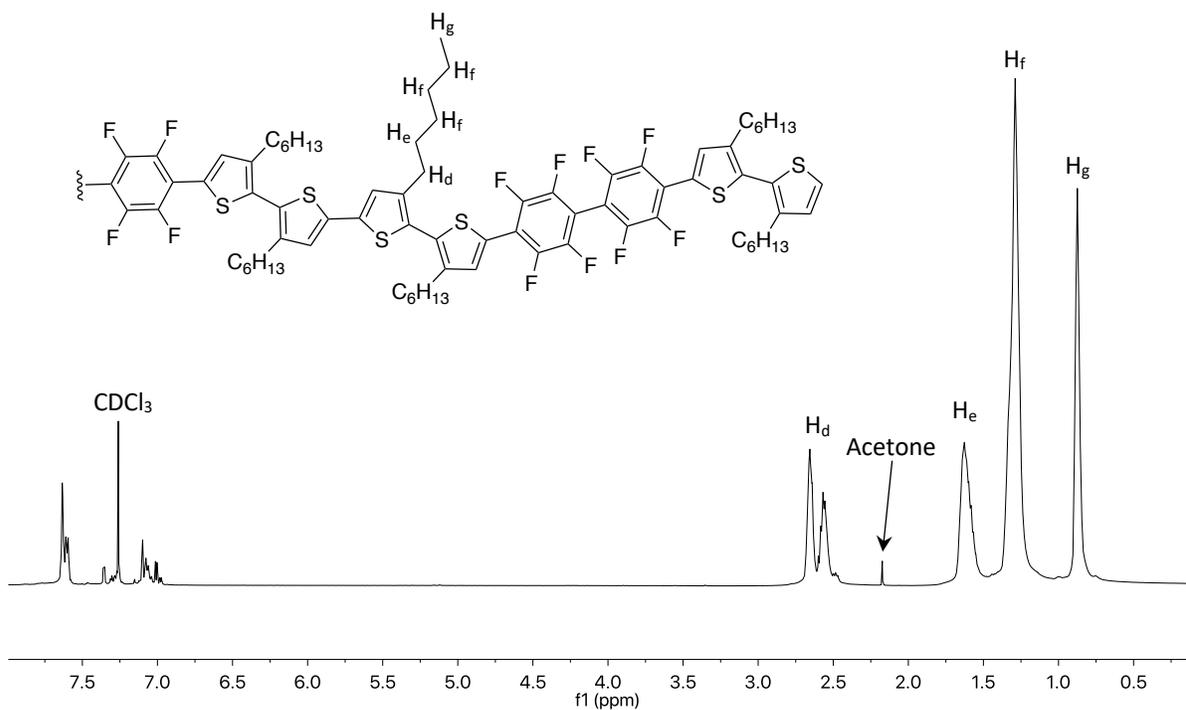


Figure S5 Example ¹H NMR (500 MHz, CDCl₃) of Polymer B at 168 h time point.

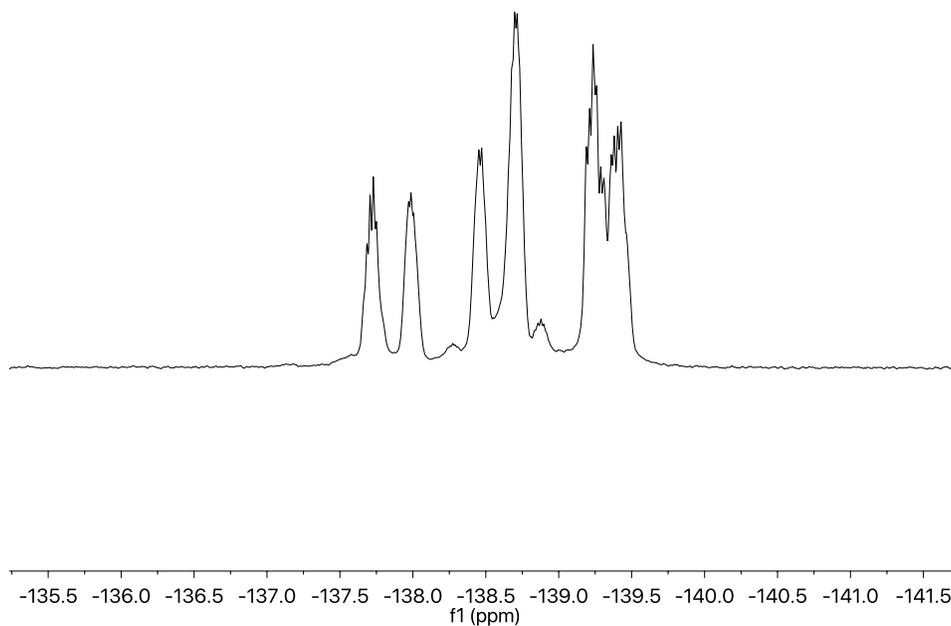


Figure S6 Example ¹⁹F NMR (470 MHz, CDCl₃) of Polymer B. The presence of multiple peaks supports that the polymer is not a perfectly alternating polymer.

Calculating % Alt, M_n , and DP Using ^1H 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.

Timepoint (h)	M_n of Polymer A (kg/mol)	DP of Polymer A	M_n of Polymer B (kg/mol)	DP of Polymer B
24	4.1	15	5.6	17
48	4.8	18	6.7	20
96	4.8	18	7.5	22
120	4.9	18	7.9	24
144	4.9	18	8.7	26
168	4.5	16	8.1	25
192	5.1	18	9.4	28

Calculation of Deuterium Incorporation (%)

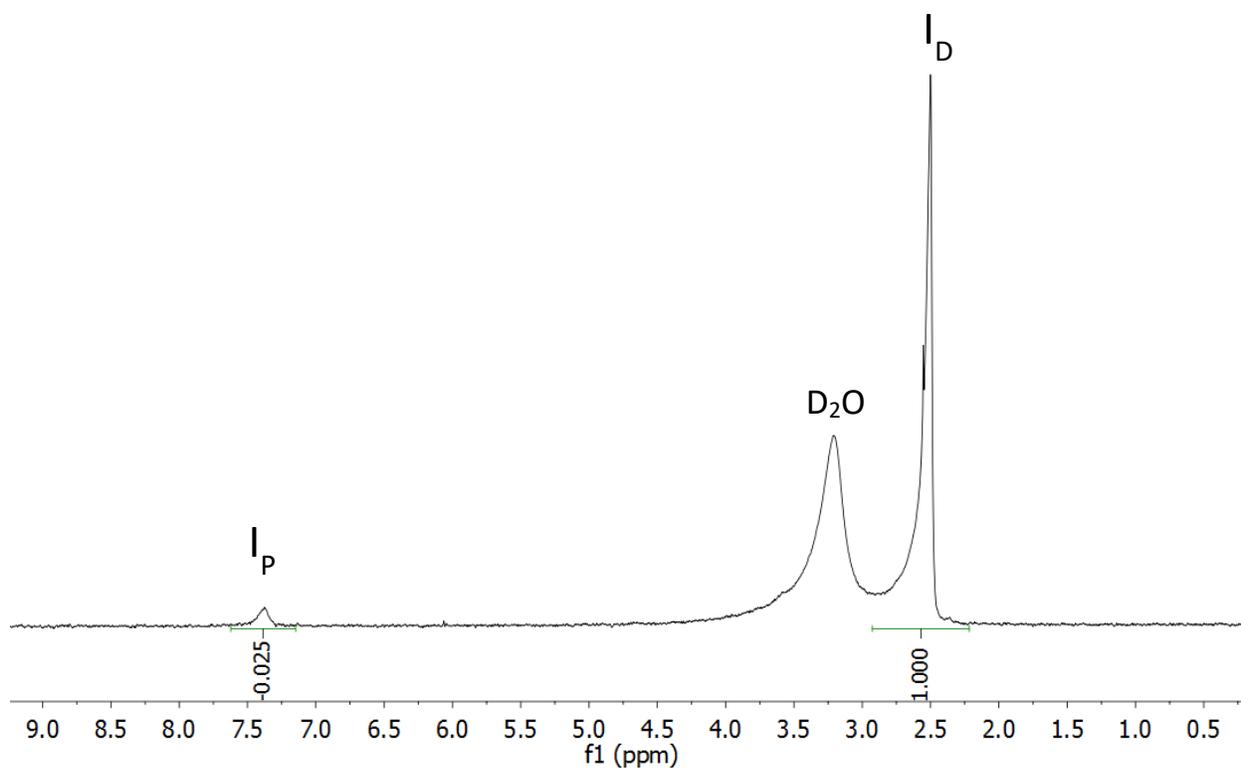


Figure S7 Example ^2H NMR of deuterated product of pentafluorobenzene reacted with AgOPiv and PPh_3AuOAc .

Deuterium incorporation was calculated using ^2H 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.

$$\text{Deuterium incorporation \%} = \frac{I_P}{I_D} \times \frac{0.141 \text{ mmol} \times 6}{0.1 \text{ mmol}} \times 100 \%$$

¹H NMR for Synthesis of PPh₃Au(I)-C₆F₅ with and without Sodium *tert*-Butoxide (NaO^tBu)

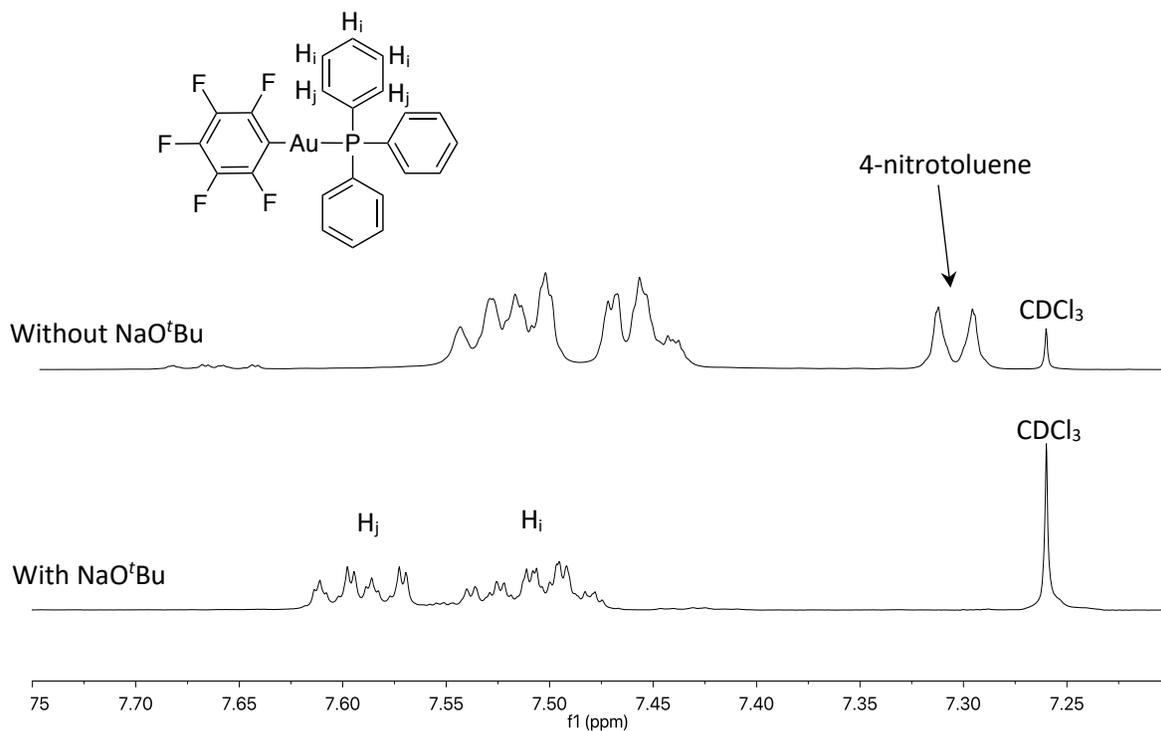
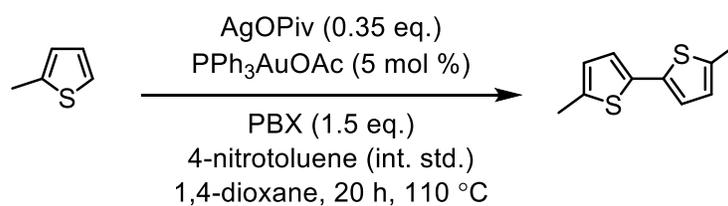


Figure S8 ¹H NMR (500 MHz, CDCl₃) spectra for synthesis of PPh₃Au(I)-C₆F₅ with and without NaO^tBu.

The complex PPh₃Au(I)-C₆F₅ could not be formed in the absence of a base, such as NaO^tBu, even when one equivalent of NaOPiv was added. The ¹H NMR of PPh₃Au(I)-C₆F₅ has been reported previously.^[4]

Control Experiment of Homo-coupling of 2-Methylthiophene



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.

¹H NMR for the Reaction Shown in Scheme 7

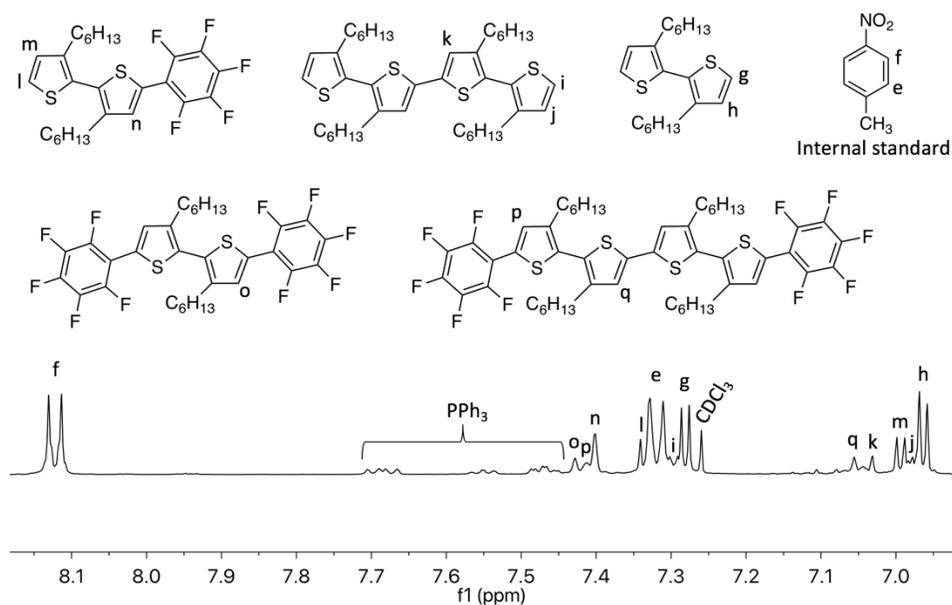


Figure S9 ¹H NMR spectrum of the reaction shown in Scheme 7 of the aromatic region.

References

- [1] X. C. Cambeiro, N. Ahlsten, I. Larrosa, *J. Am. Chem. Soc.* **2015**, *137*, 15636–15639.
- [2] D. A. Edwards, R. M. Harker, M. F. Mahon, K. C. Molloy, *Inorganica Chim. Acta* **2002**, *328*, 134–146.
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- [4] X. C. Cambeiro, T. C. Boorman, P. Lu, I. Larrosa, *Angew. Chemie Int. Ed.* **2013**, *52*, 1781–1784.