

Supporting Information

Electric-Field-Induced Coupling of Aryl Iodides with a Nickel(0) Complex

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General

All manipulations of air and moisture sensitive materials were conducted under a nitrogen atmosphere in a N₂ atmosphere drybox or on a dual manifold Schlenk line. The glassware was oven-dried prior to use. Dichloromethane and ether were degassed with nitrogen and passed through activated alumina columns and stored over 4 Å Linde-type molecular sieves. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. All other chemical reagents were purchased from commercial vendors and used without further purification. High resolution mass spectra (HR-MS) were obtained from the Columbia University Chemistry Department Mass Spectrometry Facility on a Waters XEVO G2-XS QToF mass spectrometer equipped with UPLC inlet and a LockSpray source with an electrospray ionization (ESI) probe. ¹H NMR spectra were recorded at the Columbia NMR Core Facility on a Bruker DRX400 (400 MHz) spectrometer.

Synthesis of Ni(COD)(DQ)

The synthesis of Ni(COD)(DQ) was achieved according to a reported procedure.¹ Briefly, in an inert-atmosphere glovebox a 100 mL flask was charged with duroquinone (6.54 mmol, 1 eq), Ni(COD)₂ (6.54 mmol, 1 eq), and a stir bar. Degassed, anhydrous dichloromethane (24 mL) was added to this flask and the reaction mixture was allowed to stir overnight at 45 °C. The reaction mixture was then filtered over Celite, and pentane was subsequently added to the filtrate resulting in the precipitation of a red powder (65%). This was further purified by recrystallization through vapor diffusion of pentane into a concentrated DCM solution, yielding dark red crystals. Characterization of the complex matched the literature report.¹

Synthesis of 4,4'-dithiomethylbiphenyl

The synthesis of 4,4'-dithiomethylbiphenyl was achieved according to a reported procedure.² Briefly, a 100 mL Schlenk flask was charged with 4-bromothioanisole (1.48 mmol, 1 eq), 4-(methylthio)phenylboronic acid (2.95 mmol, 2 eq), K₂CO₃ (2.95 mmol, 2 eq), and Pd(dppf)Cl₂ (0.074 mmol, 5 mol%). A 1:5 mixture of H₂O:toluene (18 mL) was degassed and transferred to the reaction flask, which was then heated to reflux at 100 °C for 1 hour. The temperature was subsequently reduced to 90 °C and the reaction mixture was stirred overnight. After cooling, the organic layer was extracted with DCM. The desired product was purified by column chromatography (DCM:hexanes) and a white solid was collected after drying under vacuum (70%). ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (d, 4H); 7.30 (d, 4H); 2.50 (s, 6H).

Ex-Situ Coupling Experiments

Ex-situ coupling reactions were carried out according to a generalized procedure: A 20 mL scintillation vial was charged with aryl iodide (0.20 mmol, 2 eq), Ni(COD)(DQ) (0.10 mmol, 1

eq), and a stir bar. The solids were dissolved in either 1 mL 1,2,4-trichlorobenzene (TCB) or DMF and the resulting solution was stirred at room temperature for 24 hours. The resulting reaction mixtures were extracted with DCM/H₂O, the organic layer was collected and dried over Na₂SO₄ then filtered. The filtrate was dried under vacuum and redissolved in CDCl₃ for ¹H NMR characterization.

Scanning Tunneling Microscopy Break Junction (STM-BJ)

Conductance measurements were collected using a custom-built scanning tunneling microscope that has previously been described in detail.³ Dilute solutions (0.1 to 10 mmol) were prepared in N,N-dimethylformamide (DMF) or 1,2,4-trichlorobenzene (TCB) solution. Au tips were prepared by driving a mechanically cut tip through Apiezon wax.⁴ One-dimensional (1D) conductance histograms were generated from logarithmic bins (100/decade), and two-dimensional (2D) histograms were generated with logarithmic bins for the conductance axis (100/decade) and linear bins (1000/nm) for the displacement axis. Displacement profiling of the molecular conductance feature in the two-dimensional histograms was applied to determine junction length.

Electrochemical Measurements

Electrochemical measurements were performed with a three-electrode configuration on a Bio-Logic VMP-3 potentiostat. Dimethylformamide was used as the solvent in analogy to STM-BJ studies and tetrabutylammonium hexafluorophosphate (0.1 M) was included as electrolyte. A polished glassy carbon stick electrode was applied as a working electrode, with a platinum wire counter electrode. A silver wire pseudo-reference electrode was used and reported potentials are referenced to an internal ferrocene/ferrocenium redox couple.

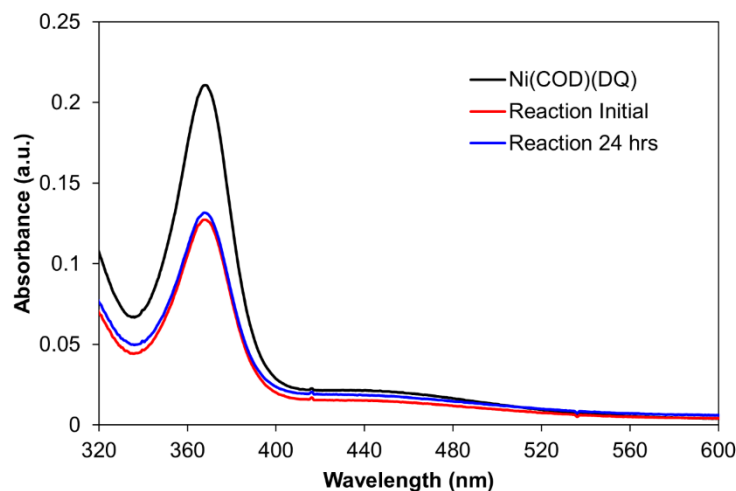


Figure S1. UV-Vis spectra of 0.1 mmol Ni(COD)(DQ) in DMF (red trace), 0.1 mmol Ni(COD)(DQ) + 1 eq. p-iodothioanisole in DMF (red trace), and this mixture after stirring at RT for 24 hours (blue trace).

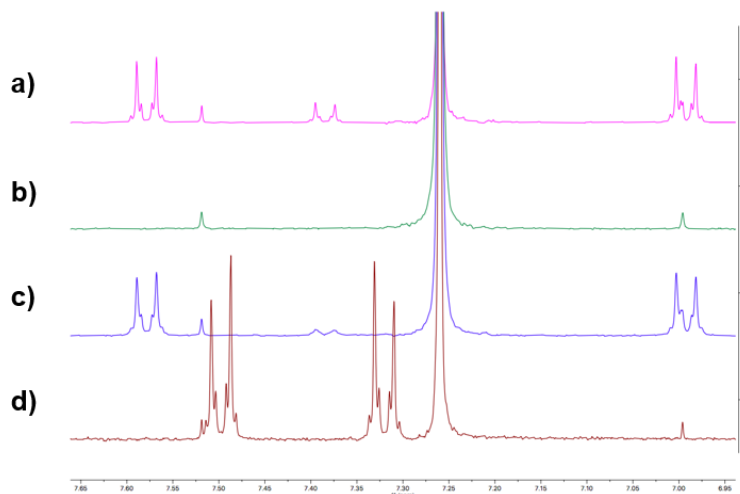


Figure S2. ^1H NMR spectra collected in CDCl_3 solvent for (a) a commercial sample of p-iodothioanisole, (b) $\text{Ni}(\text{COD})(\text{DQ})$, (c) a mixture of p-iodothioanisole and $\text{Ni}(\text{COD})(\text{DQ})$ in DMF stirred at room temperature for 24 hours, and (d) 4,4'-dithiomethylbiphenyl.

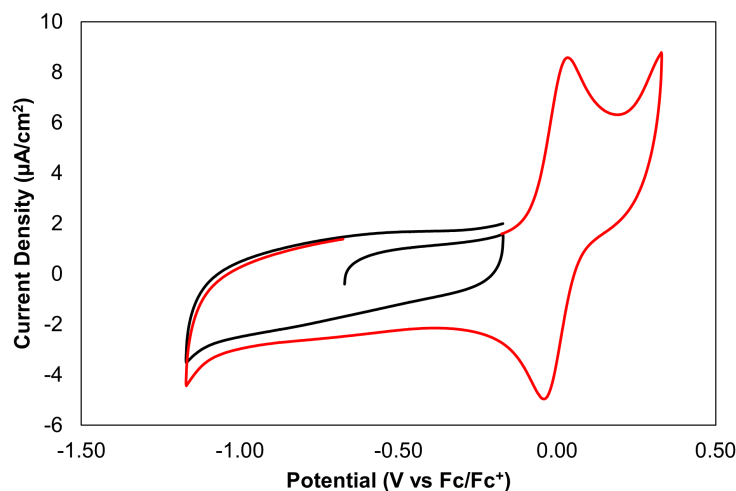


Figure S3. Cyclic voltammetry studies of a solution containing of 0.2 mM p-iodothioanisole, 0.1 mM $\text{Ni}(\text{COD})(\text{DQ})$, and 0.1 M $[\text{NBu}_4][\text{PF}_6]$ supporting electrolyte in DMF in the absence (black) and presence (red) of 0.1 mM internal ferrocene reference. The absence of any clear redox feature in the black trace indicates that no Faradaic electron transfer occurs between the polarized electrode and either the Ni complex or the aryl iodide substrate, refuting the possibility of an electrochemical transformation in the STM-BJ environment.

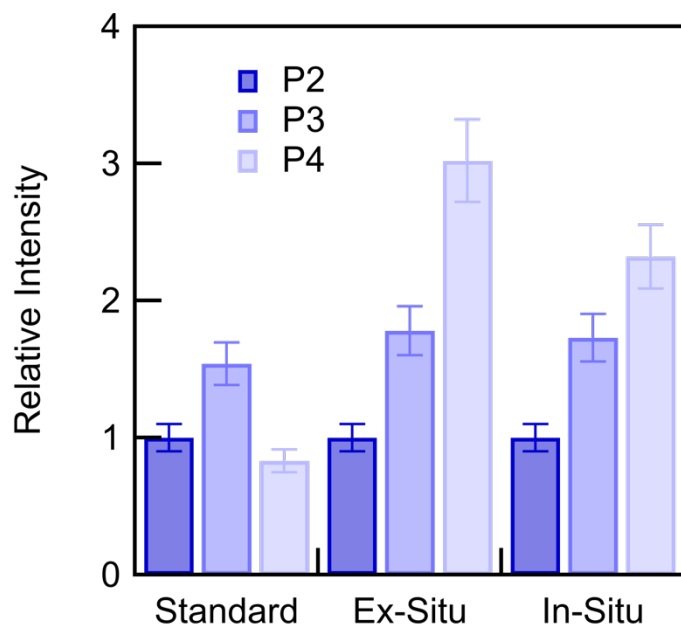


Figure S4. HRMS signal intensities for 4,4'-dithiomethylbiphenyl (P2), 4,4'-dithiomethylterphenyl (P3), and 4,4'-dithiomethylquaterphenyl (P4) measured in: a 100 μ M 1:1:1 (P2:P3:P4) standard sample (left), a sample from an ex-situ reaction with 1 eq Ni(COD)₂, 1 eq p-iodothioanisole, and 1eq 4-iodo-4'-thiomethylbiphenyl (center), and the STM-BJ reaction mixture with Ni(COD)(DQ) studied in TCB at 100 mV bias for 24 hours (right).

References:

- (1) Tran, V. T.; Li, Z. Q.; Apolinar, O.; Derosa, J.; Joannou, M. V.; Wisniewski, S. R.; Eastgate, M. D.; Engle, K. M. Ni(COD)(DQ): An Air-Stable 18-Electron Nickel(0)-Olefin Precatalyst. *Angew Chem Int Ed Engl* **2020**, *59* (19), 7409-7413. DOI: 10.1002/anie.202000124.
- (2) Haug, W. K.; Wolfson, E. R.; Morman, B. T.; Thomas, C. M.; McGrier, P. L. A Nickel-Doped Dehydrobenzoannulene-Based Two-Dimensional Covalent Organic Framework for the Reductive Cleavage of Inert Aryl C-S Bonds. *J Am Chem Soc* **2020**, *142* (12), 5521-5525. DOI: 10.1021/jacs.0c01026.
- (3) Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. Dependence of single-molecule junction conductance on molecular conformation. *Nature* **2006**, *442* (7105), 904-907. DOI: 10.1038/nature05037.
- (4) Nagahara, L. A.; Thundat, T.; Lindsay, S. M. Preparation and Characterization of STM Tips for Electrochemical Studies. *Rev. Sci. Instrum.* **1989**, *60* (10), 3128-3130.