Cross-Coupling Polymerization at Iodophenyl Thin Films Prepared by Spontaneous Grafting of a Diazonium Salt

Nicholas Marshall, Andres Rodriguez

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Development of a method for the surface-initiated Kumada cross-coupling polymerization based on 4-iodophenyldiazonium salt thin films, and use of this method to make very thick polythiophene brushes.

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Cross-coupling polymerization at iodophenyl thin films prepared by spontaneous grafting of a diazonium salt

Nicholas Marshall¹ and Andres Rodriguez²

¹Department of Chemistry and Physics, University of South Carolina Aiken, 471 University Parkway, Aiken, SC 29801, USA
²College of Pharmacy, Medical University of South Carolina, 280 Calhoun Street, Charleston, SC 29425, USA

Corresponding author:
Nicholas Marshall¹

Email address: nicholasm@usca.edu

ABSTRACT

Cross-coupling at aryl halide thin films has been well-established as a technique for the surface-confinement of the Kumada catalyst transfer polymerization (KCTP) reaction. The spontaneous grafting of 4-iodobenzenediazonium tetrafluoroborate on gold substrates creates a durable thin film which is effective as a substrate for cross-coupling reactions including the surface-initiated KCTP reaction. Using cyclic voltammetry of a surface-coupled ferrocene derivative, we have measured initiator surface coverage produced by oxidative addition of Pd(t-Bu₃P)₂ and used the resulting initiator to prepare thick, well-defined polythiophene thin films.

INTRODUCTION

Since the development of the first polyacetylenes by Shirakawa and MacDiarmid in the 1970s, (Chiang et al. (1977, 1978)) applications of pi-conjugated polymers (CPs) have proliferated. A number of refined synthetic approaches for forming these polymers have been developed. CPs based on arene repeat units are the single largest category of CP with current practical applications, due to the inherent stability of the aromatic system vs. oxidation. To prepare polyarenes, oxidative polymerization approaches are common. (Kaloni et al. (2017); Niemi et al. (1992)) Oxidative polymerization is difficult to control and applicable only to electron-rich arene monomers. More recently, cross-coupling strategies have been developed, (Yamamoto (2002); Heeger (2001)) most commonly coupling of a aryl dihalide with an arene bearing two nucleophilic groups, e.g., an “AA/BB” strategy. Stille and Suzuki coupling are commonly employed in these syntheses. (Bao et al. (1999); Argun et al. (2004),Yiu et al. (2012)) The single greatest refinement in the cross-coupling synthesis of polyarene CPs came in the mid-2000s from the Yokozawa and McCullough groups, (Yokoyama and Yokozawa (2007); Sheina et al. (2004)) in which “AB” monomers were prepared by monometallation of an aryl dihalide, most commonly through magnesium-halogen exchange to prepare an arylmagnesium halide monomer. This modification yielded a dramatic improvement in polydispersity of the prepared polymers, especially polythiophenes and poly(p-phenylene). The improvement is attributed to a change in mechanism, from a typical cross-coupling catalytic cycle to the so-called “catalyst-transfer” (CT) mechanism. (Miyakoshi et al. (2005)) In this mechanism, the zerovalent, coordinatively unsaturated transition metal does not dissociate from the growing polymer chain, but remains complexed to the pi-system. (Figure 1) Due to this complexation, the zerovalent center reacts next with the halide endgroup of the same polymer chain, and chain-growth, pseudoliving polymerization ensues. (Bryan and McNeil (2013))

The existence of this CT effect has been borne out by a number of theoretical studies, (He et al. (2018)) as well as exploits in which CTP is used to prepare block copolymers and end-functionalized polymers. (Zhang et al. (2018); Yokozawa and Yokoyama (2009); Aplan and Gomez (2017)) Many of the
most common applications of CPs involve their deposition in the form of thin films, including uses in photovoltaics, electrochromics, and sensors. (Marshall et al. (2011))

In the late 2000s, we and others used CTP to prepare conjugated polymer films grafted from a surface (SI-CTP). (Sontag et al. (2009)) Typically, this feat is accomplished by formation of a self-assembled monolayer (SAM) bearing an aryl halide, followed by reaction of the halide film surface with a zerovalent metal precatalyst to form a surface-bound metal complex. Thin films prepared from silanes are most commonly used in the preparation of the aryl halide film. This approach is reasonably effective and many interesting surface structures have been prepared using it. However, limitations of silane-based initiators exist; purification of these materials is often problematic, the surface produced is highly variable based on difficult-to-control factors such as moisture content, and the most effective coupling agents for SAM formation contain a long central alkyl chain which limits electronic coupling between the surface and the endgroup, an undesirable property for electronic applications. So, we sought to develop a more convenient initiator system for a SI-CTP reaction, specifically the surface-initiated Kumada polymerization (SI-KCTP).

Reductive electrografting of aryl diazonium salts is well-established as a surface modification protocol. (Mahouche-Chergui et al. (2011); Assresahen et al. (2015)) While careful controls such as use of antioxidant additives (Anariba et al. (2003); Menanteau et al. (2013)) or incorporation of a bulky protecting group (Combellas et al. (2008)) are necessary to ensure formation of a well-defined monolayer, this method is known to form highly functionalized and durable thin films composed of a conductive arene multilayer. (Lee et al. (2012)) While deposition of thin films from aryldiazonium salts using electrochemical reduction of the diazonium salt is a well-known technique for surface functionalization, spontaneous reaction of aryldiazonium salts with a surface is less common. However, a number of groups have explored this approach in recent years. (Stewart et al. (2004); Podvorica et al. (2009); Mesnage et al. (2012)) Terminal functional groups (as the para substituent) which have been deposited using a spontaneous method include NO₂, (Laurentius et al. (2011); Cullen et al. (2012)) COOH, (Polsky et al. (2008)) n-alkyl, (Combellas et al. (2005a)) perfluoroalkyl (Combellas et al. (2005b)) diazonium, (Marshall et al. (2018)) and amine (Kesavan and Abraham John (2014)). In particular, halide-functionalized thin films formed by spontaneous diazonium grafting from organic solutions have not been reported, and only a few (2,4,6-trichlorophenyl and 4-bromophenyl) (Mesnage et al. (2012)) from aqueous solution. The Tour group has prepared a great variety of conjugated linkers deposited spontaneously from organic solvents, particularly on silicon surfaces. (Kosynkin and Tour (2001))

Most work in this area uses aqueous solutions of the diazonium salts, exploiting the inherent instability of arenediazonium salts in water due to diazonium hydrolysis to diazohydroxide compounds. (Lewis and Johnson (1960)) Diazonium salt hydrolysis reliably forms thin films on metallic, oxide, and carbon surfaces. (Combellas et al. (2005a); Podvorica et al. (2009); Lehr et al. (2010); Berisha et al. (2016)) These films contain a substantial fraction of azo R-N=N-R’ linkages, and XPS evidence indicates that the aryl film is sometimes linked to metal surfaces through a nitrogen-metal bond. (Combellas et al. (2005a)) However, evidence is beginning to emerge that spontaneous deposition in acetonitrile (and likely other polar aprotic solvents) proceeds by a different mechanism, possibly by direct Au catalysis of C-N₂⁺ bond

Figure 1. The Kumada catalyst-transfer polymerization (CTP) of a magnesiated dihaloarene proceeds in a chain-growth fashion, yielding a polyarene chain bound to the initiator.
cleavage yielding C-Au bonds. (Mesnage et al. (2012)) Bolstering this hypothesis, we have found in this work and past studies that arenediazonium-based films formed spontaneously from acetonitrile generally do not contain any nitrogen at all, in sharp contrast to aqueous-based films driven by diazohydroxide deposition.

As a component of this work, we needed to demonstrate the spontaneous grafting of the aryldiazonium halide 4-iodobenzenediazonium tetrafluoroborate, and demonstrate that the resulting layer reacts to form a surface-bound initiator for SI-KCTP. We found that 4-iodobenzenediazonium salt spontaneously forms a thin film at a clean gold surface, and that the resulting aryl iodide layer is convenient and effective for cross-coupling. (Scheme 2) In particular, this iodoarene layer yields a high density of surface-bound Pd(II) sites active in the cross-coupling reaction as measured electrochemically using a well-known ferrocenyl probe, ferrocenyl 2-(5-chloromagnesiothienyl)methane (FcCH₂ThMgCl). This surface-bound cross-coupling initiator also reacts effectively with a thiophene AB monomer to yield polythiophene brushes.

![Figure 2](image.png)

Figure 2. The aryl diazonium salt 4-iodobenzenediazonium tetrafluoroborate reacts spontaneously with freshly cleaned Au surfaces to yield an aryl iodide-functionalized surface.

![Figure 3](image.png)

Figure 3. Reaction of an aryl iodide layer on gold with Pd(0) followed by Grignard reagents yields a ferrocene-functionalized layer with a Fc Grignard reagent, and a thick polythiophene film with a metallated A-B monomer in the SI-KCTP reaction.

In this work, we report a useful instance of spontaneous aryl diazonium salt grafting to a gold surface to prepare a functionalized surface which can serve as an initiator platform for the Pd-catalyzed SI-KCTP reaction. XPS survey scans of the functionalized surface revealed no nitrogen in the film, supporting the hypothesis that gold can directly catalyze the dissociation of the diazonium salt to give dinitrogen. The resulting surface has a high density of reactive groups as measured under standard conditions for evaluation of SI-KCTP initiator surfaces, and a remarkably thick, brushlike polythiophene film is formed on the surface when used in the SI-KCTP reaction. The convenience of this preparation method, and the thickness of the films formed, are promising for this particular method’s potential for device construction.

RESULTS AND DISCUSSION

Characterization of the aryl iodide pre-initiator surface

X-ray photoelectron spectroscopy of the aryl iodide-treated surface gives a satisfactory picture of its structure. Analysis of the intensity ratios of the Au 4f and C1s peaks (Figure 4) yields an estimated thickness of the thin film of 2.5 nm, consistent with other reported spontaneously grafted thin films. The signature of iodine is naturally easy to observe in XPS. After correction, the film gives a 1:8 I:C atomic ratio, when in an ideal monolayer 1:5 is expected. The shape of the C1s C-C peak is consistent with the presence of 2 Csp² species, with the higher-binding-energy, lower-intensity peak...
Figure 4. XPS of the spontaneously deposited 4-iodophenyl layer. a) Survey scan of the film reveals no nitrogen near 400 eV, and a strong Au 4f peak indicating a thin (ca. 2.5 nm) organic film. b) I 3d XPS of the film gives a strong signal. c) The breadth of the C 1s peak is consistent with two major species present.

representing the C-I species. The spectrum is consistent with that reported for cathodically electrografted 4-iodobenzenediazonium salt reported by López et al. (López et al. (2019)) Briefly, XPS of the spontaneously grafted film is consistent with a thin layer comprised primarily of Csp$^2$ atoms with some adventitious carbon, including residual carbonate from oxidative cleaning at 288.5 eV.

Initiator density estimation using cross-coupling of a ferrocene probe

While a halide-functionalized polyarene layer may have many applications, (Touzé et al. (2019)) we developed this process as an easy entry to surface-directed cross-coupling reactions. We can estimate an upper bound on the efficiency of the oxidative addition step (Figure 3 by reaction of a Pd(0) complex followed by cross-coupling with a ferrocene probe. We have previously shown that Pd(t-Bu$_3$P)$_2$, developed by Fu, (Littke (2002)) is an effective Pd(0) precatalyst for forming surface-bound initiators for Kumada catalyst transfer polymerization through oxidative addition. Reaction of this precatalyst with our spontaneously grafted aryl iodide layer, followed by quenching with the well-known ferrocene-bearing Grignard probe species FeCH$_2$ThMgCl, gave a ferrocene-coated gold surface with coverage ($\Gamma = 2.8 \times 10^{-10}$ mol/cm$^2$) consistent with a closely packed ferrocene monolayer (Lu et al. (2008)) and a very low separation between anodic and cathodic peaks consistent with a fast, ideal surface-confined electrochemical redox reaction.

The full width at half max (FWHM) of each peak is also consistent with a nearly ideal surface-confined redox couple. For contrast, we performed the same coupling reaction using an indium tin oxide substrate functionalized with the commercially available silane 4-bromophenyltrimethoxysilane. (Figure 5) The surface coverage of the resulting ferrocene layer was significantly lower, (Figure S5) and the peak-to-peak separation of the redox waves in the silane-based film indicates a slower rate of the redox reaction. Downard has correlated layer thickness of nitrophenyl groups with NO$_2$ group concentration in spontaneously deposited nitrophenyl films, giving concentrations of 6-14$\times 10^{-10}$ mol/cm$^2$. (Lehr et al. (2009)) Surprisingly, our electrochemically measured surface coverages are reasonably consistent with these values, despite the much greater steric demands of the cross-coupling reaction as over against the electrochemical reduction of a -NO$_2$ group. Overall, cyclic voltammetry of the cross-coupled aryl iodide substrate indicates efficient conversion of surface aryl iodide groups in the arenediazonium-based film to Ar-Pd(II) groups and subsequent reaction with an aryl Grignard reagent in solution, effectively proving
the formation of a surface-bound Pd(II) catalyst for Kumada coupling.

**Figure 5.** a) Cyclic voltammetry of PhI thin film after reaction with the ferrocene cross-coupling probe Fc-CH$_2$-ThMgCl shows a densely packed surface (2.8x10$^{-10}$ mol/cm$^2$) and a near-ideal surface redox couple consistent with a thin arene layer. b) A commercial bromophenyl silane yields an order of magnitude lower surface coverage, larger FWHM of redox peaks, and larger peak-to-peak separation.

An important ancillary finding of this work is that the standard procedure for forming FcCH$_2$ThMgCl), with a single equivalent of isopropylmagnesium chloride (iPrMgCl) does not completely convert the precursor halide into the probe species FeCH$_2$ThMgCl. (Figure S4) While two equivalents of iPrMgCl does accomplish this conversion, the resulting Grignard solution yields a lower surface coverage after cross-coupling than the partially converted material. (Figure S5) Groups using this procedure should be aware that this complication exists, and surface coverage values generated using this protocol should be regarded as upper bounds.

**SI-KCTP using the surface-bound initiator**

Reaction of species of the form X-Ar-MgX' with surface-bound Pd(II) and Ni(II) catalysts has been established as a state-of-the-art technique for surface-initiated chain-growth polymerization yielding polyarene films, including polythiophene films. The surface-bound Ar-PdL$_2$I complex produced from our film’s reaction with the Fu catalyst is effective in the SI-KCTP reaction, yielding a very thick (ca. 1 µm) PT film with a purple color.

The purple (as opposed to the more common red) is characteristic of PT in an extended chain conformation with a high conjugation length, indicating in this case that the chains are sufficiently close in origin point to be forced into an extended brushlike configuration. No precipitate of polymer was observed in solution after several hours. On the other hand, the surface-bound initiator produced from the reduced PEPPSI catalyst reacted within 15 minutes to yield visible red polymer suspended in the reaction vial. This sample was coated with a thinner, highly uniform red polythiophene film after reaction was complete. These observations are consistent with the N-heterocyclic carbene-based PEPPSI catalyst having a much higher reaction rate than the Fu catalyst, but being relatively weakly bound to the growing chain in the zerovalent state such that the catalyst soon dissociates, ending surface-directed chain growth of the polymer brush. Reflectance UV-visible spectroscopy of the films is consistent with this interpretation. (Figure 7) The film produced by the Fu catalyst (PT-Fu) has an intense and narrow transition redshifted from the lowest-energy absorption of the film formed by reduced PEPPSI. The redshift is due partially to a longer conjugation length in the higher molecular weight polythiophene, comparable to the most densely grafted literature reports of PT films but primarily due to the increased grafting density in the PT-Fu film relative to the PEPPSI film and to literature reports of thinner unsubstituted PT films. (C)

Densely grafted, thick brushlike PT films are purple. (Youm et al. (2016)) (Figure 6, inset) To the best of our knowledge, this is the first report in the literature of the preparation of unsubstituted PT brushes using PEPPSI or the popular Fu catalyst.

The regular decoration of physisorbed PT nanoparticles visible in Figure 6 was an unexpected discovery, since the polymer film was washed well with water and organic solvents after formation. A reasonable explanation for these interesting low-polydispersity features is that they were formed from
Figure 6. (a) SEM of a PT film produced by SI-KCTP according to Figure 2 shows a morphology consisting of a rough PT coating. Physisorbed PT particles are also visible. Inset: The PT film produced on gold is a dark purple color, indicating closely packed PT chains. (b) A lower-magnification image of the same PT film reveals that the PT film bears a regular distribution of narrow-size-distribution PT particles. EDS mapping of this region (Figure S1) shows carbon and sulfur signals associated with the film and particles, confirming the presence of polythiophenes. (c) Rigorous cleaning removes physisorbed polythiophene, but leaves the surface-bound PT brush intact. (d) Fracturing the substrate and imaging from the side gives a PT film thickness of approximately 1 µm, a remarkably thick film compared to other PT films reported from SI-KCTP.

Regardless of the origin of the nanosphere features, microscopy of the substrate produced from the reaction of polyarene films with Pd(0) complexes followed by BrThMgCl shows a roughly 1 micron thick, regular film of polythiophene which is robust to rigorous cleaning procedures. In our experience, the use of the commercially available Fu Pd catalyst is very convenient and reproducible relative to approaches based on Ni(COD)$_2$ with various ligands, and the surface coverages attained by our method are as good or better than other state-of-the-art techniques. Youm et al. (2016); Sontag et al. (2011) The film produced by the Fu catalyst is among the thickest PT films produced by coupling methods (rather than electrochemical oxidative polymerization) currently reported in the literature, and this combination of catalyst and monomer may be particularly useful for preparation of polymer films for electronic devices. The film produced by the reduced PEPPSI Pd catalyst was not as thick nor the reaction as controlled, but the fact that this approach succeeded in producing a uniform film is worth reporting, as Pd(II) complexes (and PEPPSI in particular) are much easier to handle and prepare than the air-unstable Pd(0) precatalysts. Overall, microscopy and spectroscopy of the polymerized substrates demonstrates that the spontaneously
Figure 7. Reflectance UV-vis of polythiophene films prepared using (a) (t-Bu3P)2Pd (“Fu”) and (b) PEPPSI Pd catalysts. The Fu catalyst yields a thick, densely grafted film.

grafted aryl iodide film produced from 4-iodobenzenediazonium tetrafluoroborate is an effective and mechanically/chemically robust precatalyst for the SI-KCTP reaction.

EXPERIMENTAL

General experimental remarks
Gold-coated slides were standard float glass microscope slides coated with roughly 100 nm Au on a Cr adhesion layer, purchased from Sigma-Aldrich. HPLC-grade acetonitrile was purchased from Alfa Aesar and stored over 4A molecular sieves. Other chemicals were purchased directly from well-known chemical suppliers and used as received. The ferrocene coupling agent FcCH2ThBr was prepared according to the procedure freely available in the Supporting Information of our previous report. (Sontag et al. (2011))

1,3-Bis(2,6-Diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI) was prepared according to a literature procedure. (O’Brien et al. (2006))

Synthetic procedures

Synthesis of 4-iodobenzenediazonium tetrafluoroborate.
4-iodoaniline was prepared by iodination of aniline with molecular iodine in aqueous sodium bicarbonate solution according to Vogel’s procedure, Vogel and Furniss (1989) and recrystallized from boiling heptane to yield pure yellow needles. Recrystallized 4-iodoaniline (0.54 g, 2.5 mmol) was suspended in 2 mL deionized water and cooled below 0 C in an ice/salt bath. 2 mL of concentrated HCl was added, and the reaction was stirred until it had returned to the ice bath temperature. Sodium nitrite (0.19 g, 2.8 mmol) was added in a single portion, and the reaction was stirred for 30 minutes. After this time, sodium tetrafluoroborate (0.55 g, 5 mmol) was dissolved in a minimum amount of deionized water and added to the reaction while stirring. A yellow precipitate was formed and collected by vacuum filtration, and washed with cold water, cold methanol, and diethyl ether. This product was taken up in a minimum amount of acetonitrile and re-precipitated by adding diethyl ether to yield yellow crystals, 0.090g, 28%.

Deposition of aryl iodide thin films
A 50 mM solution of freshly recrystallized 4-iodobenzenediazonium tetrafluoroborate was prepared in dry acetonitrile, typically a 10 mL sample in a clean 20 mL scintillation vial. 1-3 pieces of cut gold-coated glass slide were cleaned. Cleaning included sonication in isopropyl alcohol, washing with deionized water, followed by 5 min immersion in freshly prepared sulfuric acid/30% hydrogen peroxide "piranha" solution, 3:1 v:v. (Caution: this mixture is violently reactive, especially with organic materials; the smallest amount practical should be prepared, and piranha should be handled using exclusively glass materials in a clean, uncluttered hood. The operator should wear body protection, gloves, and face protection.) Freshly cleaned slide substrates were blown free of moisture in a stream of nitrogen gas, and added immediately to a freshly prepared iodobenzenediazonium salt solution. Substrates were allowed to stand without stirring for 1-2h, then removed and washed with copious amounts of acetonitrile and dried in a stream of nitrogen gas.
Functionalized gold substrates were stored in a covered Petri dish in lab atmosphere with no additional precautions until use.

**Surface coupling procedure**

In a nitrogen-filled glove box, 10 mM solutions of Pd initiators were prepared in toluene. Pd(t-Bu₃P)₂ solution was prepared directly from the solid, available commercially from TCI as a beige powder and yielding a faintly yellow solution. The air-stable Pd(II) complex i-Pr-PEPPSI was suspended in toluene in an amount calculated to yield a 10 mM solution, and 2 equiv. freshly titrated i-PrMgCl in 2-MeTHF was added dropwise while agitating. A clear yellow solution was obtained, which gave a grey precipitate after a few minutes. This solution was used as formed.

Grignard coupling agents were prepared by addition at room temperature while stirring in the glove box of 1.0 equivalent of freshly titrated i-PrMgCl.LiCl solution to a 50 mmol solution of the aryl halide (2,5-dibromothiophene or FcCH₂ThBr) in THF. Aliquots of the polymerization solution were saved, removed from the glove box, and quenched with water to confirm the presence of excess halide; excess i-PrMgCl is detrimental to the cross-coupling reaction.

Aryl iodide functionalized slides were placed in a Pd initiator solution within the glove box and the solution heated to 60 °C on a hot plate in a sealed vial for 2 hours. Slides were removed from the vial, washed 3x with toluene, and transferred to a 50 mM solution of Grignard reactant prepared as above (either 2-chloromagnesio-5-bromothiophene or ferrocene probe ClMgTh-CH₂-Fc) and heated to 60 °C overnight. After reaction, samples were removed from the glove box, exposed to atmosphere, and washed with THF, ethanol, water, and acetone. For samples termed “rigorously cleaned,” PT-grafted films were placed in a scintillation vial half filled with chloroform, heated to boiling for several minutes, and allowed to cool. This cycle was repeated twice. The samples were removed from the film and dried in air.

**Electrochemistry**

Cyclic voltammetry (CV) and alternating-current voltammetry were performed using a BASi PalmSens 3 potentiostat/galvanostat in a three-electrode cell configuration. A 100 mM solution of tetrabutylammonium hexafluorophosphate in dichloromethane was used as electrolyte. A silver wire pseudoreference electrode was used, and a platinum wire was used as the counter electrode. Electrochemical surface coverages were determined by direct integration of CV peaks, and are reported as an average of anodic and cathodic peaks. Surface area of electrodes was estimated by imaging of the electrode surface with a 2.83 cm² standard and image analysis using ImageJ to determine working area.

**X-ray photoelectron spectroscopy**

XPS measurements were performed in the USC Center for Engineering and Computing. The instrument used was a Kratos Axis Ultra DLD with a hemispherical analyzer and monochromator-equipped Al Kα source. The Au 4f₁/₂ peak was used as a binding energy reference at 84.0 eV; no significant charging was observed on these highly conductive substrates.

**Scanning electron microscopy**

SEM and EDX were performed on an Hitachi Cold Field Emission 8200 Series FE-SEM at the Applied Research Center, Aiken, SC, USA. A 9 kV accelerating voltage was used for typical images shown.

**Vibrational spectroscopy**

A Thermo Electron Nicolet 4700 Fourier transform IR spectrometer using a DTGS detector and fitted with a grazing angle accessory was used to collect IR spectra of thin films. Bulk IR spectra of samples were collected on a Nicolet 380 spectrometer with a Smart Orbit diamond ATR attachment. 64 scans were summed at a 4 cm⁻¹ resolution to produce a typical spectrum.

**CONCLUSIONS**

A robust aryl iodide thin film is spontaneously deposited on gold surfaces by an acetonitrile solution of 4-iodobenzenediazonium tetrafluoroborate. This is the first report of thin film formation based on an aryl halide diazonium salt which is (a) from an organic solution and (b) spontaneous rather than reductively electrografted. The resulting film contains no nitrogen, in notable contrast with spontaneously deposited films from aqueous diazonium salt solutions. The aryl iodide film can be efficiently reacted.
with Pd(0) complexes to give surface-bound Pd(II) initiator complexes, including a complex generated in situ from the well-known air-stable Pd(II) cross-coupling catalyst i-Pr-PEPPSI. The surface-bound Pd(II) complex produced from the “Fu catalyst,” Pd(t-Bu3P)2, initiates polymerization with 2-chloromagnesio-5-bromothiophene solution to yield densely grafted and durable polythiophene brushes up to 1 micron in thickness. This initiator system is synthetically convenient and is likely to find use in organic electronic device construction.

ADDITIONAL INFORMATION AND DECLARATIONS

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Supporting information for:

Cross-coupling polymerization at iodophenyl thin films prepared by spontaneous grafting of a diazonium salt

Nicholas Marshall

University of South Carolina Aiken, Department of Chemistry and Physics.

471 University Parkway, Aiken, SC, 29801, USA. Tel: 1.803.641.3409; E-mail: nicholasm@usca.edu.http://orcid.org/0000-0001-8048-0857
Figure S1. EDS element mapping of the cracked substrate in Fig. 7b. The carbon and sulfur signals are strongly associated with the film.
Figure S2. EDS element mapping and spectrum of the cleaned substrate in Fig. 7c.
Figure S3. SEM micrograph of the PT film produced by the PEPPSI catalyst.
**Figure S4.** TLC of water-quenched aliquots of the magnesiated ferrocene probe $\text{FcCH}_2\text{ThMgCl}$ as prepared under various conditions. Solutions with unconverted $\text{FcCH}_2\text{ThBr}$, including the 1h/1eq. sample, underwent cross-coupling with the aryl iodide surface as measured by cyclic voltammetry.
**Figure S5.** Cyclic voltammetry of aryl iodide-functionalized substrates coupled with ferrocene probe FcCH₂ThMgCl prepared under various conditions. Despite lower conversion, use of an excess of FcCH₂ThBr yields much higher surface coverage of ferrocenyl groups than an excess of iPrMgCl. Curves correspond to coupling solutions "1h/1eq" (red) and "1h/3eq" (black), respectively, in Figure S4.
