

## **Supporting Information:**

### **Continuous Assembly of Polymers via Solid Phase Reactions**

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## Materials

Allyl bromide (99%), [1,3-bis(diphenylphosphino)propane]dichloronickel(II), 3-bromothiophene (97%), calcium hydride ( $\text{CaH}_2$ ), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), 4-(dimethylamino)pyridine (DMAP,  $\geq 99\%$ ), ethyl vinyl ether (EVE, 99%), Grubbs catalyst (2<sup>nd</sup> generation), *N*-bromo succinimide (99%), 5-norbornene-2-carboxylic acid (mixture of *endo* and *exo*, 98%), poly(ethylene glycol) (PEG) ( $M_w \sim 400$  kDa), poly(ethylene imine) (PEI) ( $M_w \sim 25$  kDa), *tert*-butylmagnesium chloride solution (1 M in THF), 3-(2-hydroxyethyl)thiophene (99%) and 1,3-bis(trimethylsilyl)urea (95%) were obtained from Aldrich and used without further purification. Metathesis catalyst ( $\text{IMesH}_2$ )(Cl)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>Ru=CHPh **1** was prepared from 2<sup>nd</sup> generation Grubbs catalyst as described in the literature.<sup>1</sup> Pyridine was obtained from Scharlau and used without further purification. Magnesium sulfate (MgSO<sub>4</sub>, anhydrous), *n*-hexane, toluene, isopropanol and ethanol were obtained from Merck and used directly. Diethyl ether (DEE), *N,N*-dimethylformamide (DMF) and sodium hydroxide (NaOH) were obtained from Chem-Supply and used directly. Anhydrous, deoxygenated dichloromethane (DCM) and tetrahydrofuran (THF) were obtained by distillation under argon from  $\text{CaH}_2$  and sodium benzophenone ketyl, respectively. Deuterated chloroform (CDCl<sub>3</sub>) and methanol (CD<sub>3</sub>OD) were obtained from Cambridge Isotope Laboratories. High-purity water with a resistivity greater than 18 M $\Omega$ ·cm was obtained from an in-line Millipore RiOs/Origin water purification system. Silicon wafers (MMRC Pty. Ltd., Melbourne, Australia) were cut to approximately 1 × 1 cm slides and cleaned with Piranha solution (sulfuric acid:hydrogen peroxide = 7:3) – *Caution! Piranha solution is highly corrosive and extreme care should be taken during preparation and use.* The slides were then sonicated in isopropanol:water (1:1) solution for 15 min and finally heated to 60 °C for 20 min in RCA solution (water:ammonia:hydrogen peroxide = 5:1:1). The slides were washed thoroughly with Milli-Q water between each step.

## Characterization methods

Gel permeation chromatography (GPC) data was obtained using a Viscotek GPC Max VE2001 solvent/sample module equipped with a Viscotek VE3580 refractive index detector. Toluene was used as the eluent with a 200  $\mu\text{L}$  sample volume injection. Samples were passed through three 30 cm, PL gel (5  $\mu\text{m}$ ) mixed C columns and one 30 cm, PL gel (3  $\mu\text{m}$ ) mixed E column at 0.6  $\text{mL}\cdot\text{min}^{-1}$ . Molecular mass distributions were calculated relative to narrow polystyrene reference standards.

$^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy was conducted on a Varian Unity 400 MHz spectrometer at 400 MHz using deuterated solvent as reference and at a sample concentration of *ca.* 20  $\text{mg}\cdot\text{mL}^{-1}$ .

Atomic force microscopy (AFM) images of air-dried ssCAP<sub>ROMP</sub> films on silicon wafers were acquired with an MFP-3D Asylum Research instrument. Typical scans were conducted in AC mode with ultrasharp SiN gold-coated cantilevers (MikroMasch, Bulgaria). Image processing and surface roughness analysis were performed using the Nanoscope and Igor Pro software programs, respectively. CAP film thicknesses were estimated by film scratching (mechanical removal) and by tracing a profile along the film and the scratched zone. The thickness measurements reported represent mean values over 3 different analysis sites per substrates.

Differential scanning calorimetry (DSC) analysis was carried out with a PerkinElmer Pyris-1 DSC instrument. **P1** first heated from 0 to 300  $^{\circ}\text{C}$  at a heating rate of 20  $^{\circ}\text{C}\cdot\text{min}^{-1}$ , then cooled to 0  $^{\circ}\text{C}$  at a cooling rate of 20  $^{\circ}\text{C}\cdot\text{min}^{-1}$ , and **P2** heated from  $-70$  to 150  $^{\circ}\text{C}$  at a heating rate of 20  $^{\circ}\text{C}\cdot\text{min}^{-1}$ , then cooled to  $-70$   $^{\circ}\text{C}$  at a cooling rate of 20  $^{\circ}\text{C}\cdot\text{min}^{-1}$ .

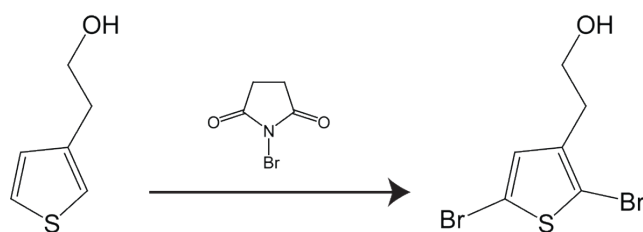
MALDI ToF MS was performed on a Bruker Autoflex III Mass Spectrometer operating in positive/linear mode. The analyte, matrix (DCTB) and cationisation agent KTFA were dissolved in THF at concentrations of 10, 10 and 1  $\text{mg}\cdot\text{mL}^{-1}$ , respectively, and then mixed in

a ratio of 10:1:1. 0.3 mL of this solution was then spotted onto a ground steel target plate, and the solvent was allowed to evaporate prior to analysis. FlexAnalysis (Bruker) was used to analyze the data.

## Experimental Methods

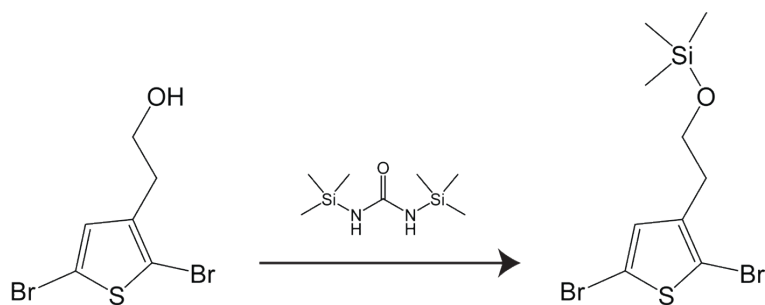
### 1. Monomer and polymer preparation

#### 1.1 Synthesis of 2,5-dibromo-3-(2-hydroxyethyl)thiophene **1**



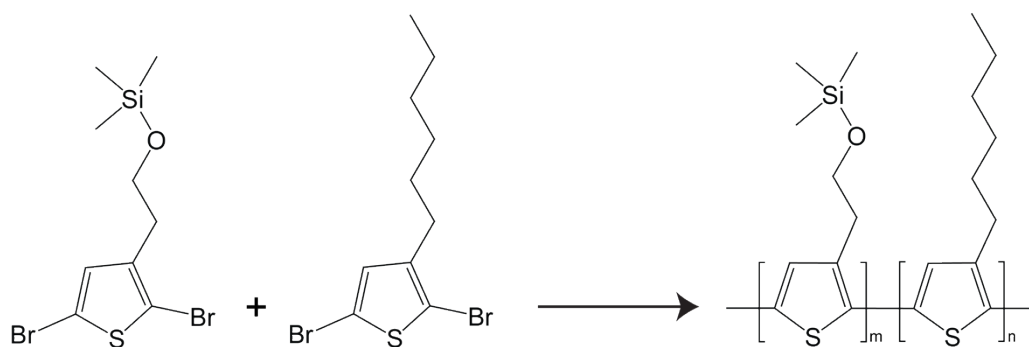
To a solution of 3-(2-hydroxyethyl)thiophene (1.0 g, 7.801 mmol) in DMF (9.4 mL), a solution of a *N*-bromosuccinimide (NBS) (3.055 g, 17.162 mmol) in DMF (9.4 mL) was added dropwise at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and stirred for a further 48 h. The solution was then added to an ice cooled 2.5 M NaOH solution (9.4 mL) and left to stirred for another 15 min before extraction with diethyl ether (DEE) (5 × 9.4 mL). The combined organic extracts were washed with 2.5 M NaOH solution (14 mL), H<sub>2</sub>O (3 × 14 mL), and brine (14 mL), dried over MgSO<sub>4</sub> and concentrated *in vacuo* (20 mbar, 30 °C) to afford 2,5-dibromo-3-(2-hydroxyethyl)thiophene **1** as a yellow liquid, 1.99 g (89%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta_{\text{H}}$  6.88 (*s*, 1H, =CH), 3.82 (*q*, 2H, CH<sub>2</sub>OH), 2.81 (*t*, 2H, CCH<sub>2</sub>), 1.45 (*t*, 1H, OH) ppm.

#### 1.2 Synthesis of 2,5-dibromo-3-(2-(trimethylsiloxy)ethyl)thiophene **2**



1,3-Bis(trimethylsilyl)urea (0.68 g, 3.3 mmol) was added to a solution of **1** (1.9 g, 6.6 mmol) in anhydrous dichloromethane (DCM) (13 mL). The reaction mixture was heated at reflux for 15 h under argon. After cooling to room temperature, the mixture was filtered and concentrated *in vacuo* (20 mbar, 40 °C) to afford **2** as a yellow liquid, 2.14 g (90%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ<sub>H</sub> 6.84 (s, 1H, =CH), 3.71 (t, 2H, CH<sub>2</sub>O), 2.75 (t, 2H, CCH<sub>2</sub>), 0.086 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>) ppm.

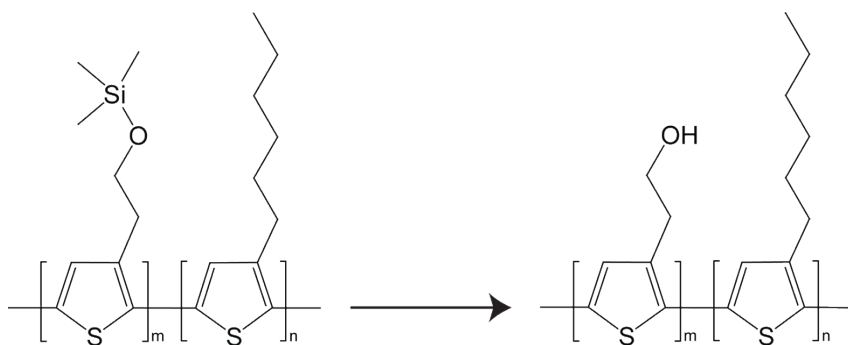
### 1.3 Synthesis of Poly[3-hexylthiophene-co-3-(2-(trimethylsiloxy)ethyl)thiophene][P3HT-co-T2OSi]



1 M *t*-BuMgCl in THF (1 mL, 1 mmol) was added dropwise to a solution of **2** (0.361 g, 1 mmol) in anhydrous THF (8.1 mL) under nitrogen. Separately, a solution of 1 M *t*-BuMgCl in THF (5.8 mL, 5.8 mmol) was added dropwise under nitrogen to a solution of 2,5-dibromo-3-hexylthiophene (1.853 g, 5.7 mmol) in anhydrous THF (23.2 mL) (2,5-dibromo-3-hexylthiophene was prepared from 3-bromothiophene using literature methods).<sup>2</sup> Both reaction mixtures were stirred at room temperature for 18 h. After complete activation of Grignard monomer was confirmed by NMR, the solution of **2** was transferred to the solution of 2,5-dibromo-3-hexylthiophene using a cannula. Ni(dppp)Cl<sub>2</sub> (28 mg, 0.514 mmol) was then added and the mixture was stirred at 70 °C under nitrogen for 20 h. After cooling to room temperature the mixture was precipitated into methanol (300 mL). The precipitate was washed with methanol (2 × 80 mL) and petroleum benzene (4 × 80 mL), isolated by centrifugation, and dried *in vacuo* (0.05 mbar, 45 °C) to yield polymer [P3HT-co-T2OSi] as a purple solid, 0.705 g (33%); consisting of 87 mol% of 3HT and 13 mol% of T2OSi repeat units; GPC-RI (Toluene): *M<sub>w</sub>* = 28.3 kDa, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.3; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ<sub>H</sub> 7.04 (s, 1H, =CH in T2OSi unit), 6.99 (s, 1H, =CH in 3HT unit), 3.89 (t, 2H, CH<sub>2</sub>O in T2OSi unit), 3.09 (t, 2H, CCH<sub>2</sub> in T2OSi unit), 2.81 (t, 2H, CCH<sub>2</sub> in 3HT unit), 1.78-1.63 (m,

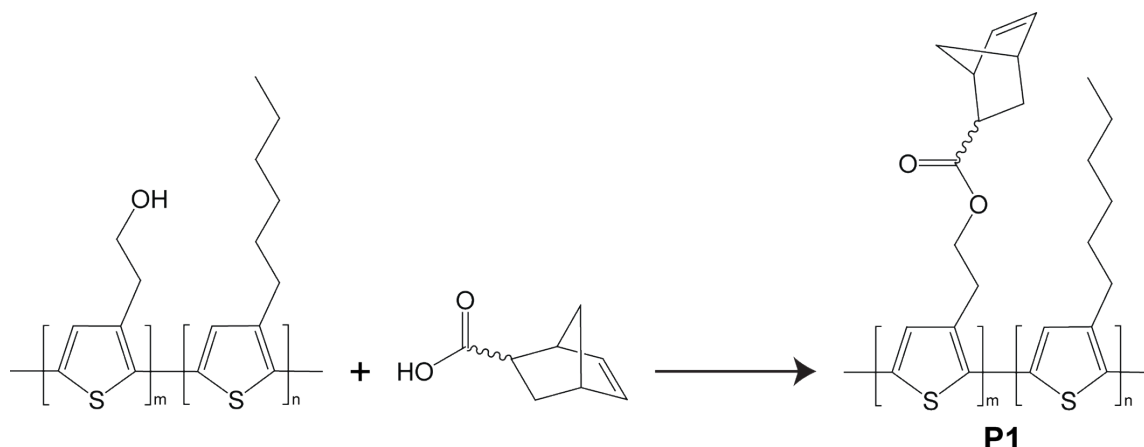
2H, CCH<sub>2</sub>CH<sub>2</sub> in 3HT unit), 1.50-1.23 (*m*, 6H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> in 3HT unit), 0.98-0.83 (*m*, 3H, CH<sub>3</sub> in 3HT unit), 0.13 (*s*, 9H, Si(CH<sub>3</sub>)<sub>3</sub> in T2OSi unit) ppm.

#### 1.4 Synthesis of Poly[3-hexylthiophene-co-3-(2-hydroxyethyl)thiophene] [P3HT-co-T2OH]



To a solution of [P3HT-*co*-T2OSi] (0.685 g, 4.02 mmol) in THF (50 mL), 0.2 M HCl in methanol (9.9 mL) was added dropwise for 2 h under argon, and the mixture was stirred at 50 °C under argon for a further 15 h. The mixture was cooled to room temperature, neutralized with 5% KOH in methanol (200 µL), and then precipitated into methanol (300 mL). The precipitate was washed with methanol (3 × 80 mL), isolated by centrifugation, and dried *in vacuo* (0.05 mbar, 45 °C) to yield [P3HT-*co*-T2OH], 0.623 g (96%), consisting of 87 mol% of 3HT and 13 mol% of T2OH repeat units; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C) δ<sub>H</sub> 7.05 & 7.03 (2*s*, 1H, =CH in T2OH unit), 6.98 (*s*, 1H, =CH in 3HT unit), 3.97 (*t*, 2H, CH<sub>2</sub>OH in T2OH unit), 3.12 (*t*, 2H, CCH<sub>2</sub> in T2OH unit), 2.81 (*t*, 2H, CCH<sub>2</sub> in 3HT unit), 1.77-1.64 (*m*, 2H, CCH<sub>2</sub>CH<sub>2</sub> in 3HT unit), 1.50-1.23 (*m*, 6H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> in 3HT unit), 0.98-0.83 (*m*, 3H, CH<sub>3</sub> in 3HT unit) ppm.

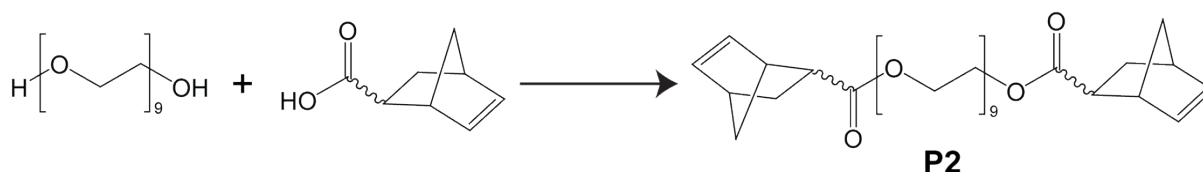
*1.5 Synthesis of Poly[3-hexylthiophene-co-3-(2-(5-norbornyl-2-carboxy) ethyl)thiophene] [P3HT-co-T2ONB] P1*



[P3HT-co-T2OH] (0.623 g, 0.48 mmol: T2OH unit) and 5-norbornene-2-carboxylic acid (0.133 g, 0.97 mmol) were dissolved in anhydrous THF (80 mL) under argon, followed by the addition of DCC (0.2 g, 0.97 mmol) and DMAP (11.8 mg, 0.97 mmol). The reaction solution was stirred at room temperature for 24 h and then added dropwise to methanol (500 mL). The precipitate was washed with methanol ( $3 \times 100$  mL), isolated by centrifugation and dried *in vacuo* (0.05 mbar, 45 °C) to yield [P3HT-co-T2ONB] as a purple solid, 0.588 g (87%). The obtained [P3HT-co-T2ONB] (0.5 g) was added to a Soxhlet thimble and firstly extracted with methanol for 1 h to remove any monomer and low molecular weight impurities. The polymer was then extracted with DCM for 20 h to remove the low molecular weight fraction of [P3HT-co-T2ONB], followed by  $\text{CHCl}_3$  for another 16 h to obtain the higher molecular weight fraction. The  $\text{CHCl}_3$  fraction was concentrated and dried *in vacuo* (0.05 mbar, 45 °C) to yield higher molecular weight [P3HT-co-T2ONB] **P1** as a purple solid 0.3 g; GPC-RI (Toluene):  $M_w = 35.9$  kDa,  $M_w/M_n = 1.2$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta_{\text{H}}$  7.08-7.02 (*m*, 1H, =CH in T2ONB unit), 6.99 (*s*, 1H, =CH in 3HT unit), 6.20-6.08 & 5.89-5.83 (*m*, 2H, CH=CH), 4.44-4.29 (*m*, 2H,  $\text{CH}_2\text{O}$ ), 3.28-3.08 (*m*, 2H,  $\text{CCH}_2$  in T2ONB unit), 2.81 (*t*, 2H,  $\text{CCH}_2$  in 3HT unit), 1.80-1.63 (*m*, 2H,  $\text{CCH}_2\text{CH}_2$ ), 1.50-1.23 (*m*, 6H,  $(\text{CH}_2)_3\text{CH}_3$ ), 1.00-0.81 (*m*, 3H,  $\text{CH}_3$ ) ppm. Pendant norbornene functionality was 13.5% as determined by  $^1\text{H}$  NMR spectroscopic analysis.  $T_g$  was 147 °C as determined by DSC.



### 1.6 Synthesis of bisnorbornyl terminated poly(ethylene glycol) **P2**



PEG (2.00 g, 5 mmol), 5-norbornene-2-carboxylic acid (4.13g, 20 mmol), DCC (4.13 g, 20 mmol) and DMAP (0.244 g, 2 mmol) were dissolved in anhydrous THF (60 mL) and stirred at room temperature for 24 h. The mixture was centrifuged and the supernatant was concentrated *in vacuo* (20 mbar, 40 °C), redissolved in DCM (15 mL), and washed with 1 mM HCl (Ph 3) (2 × 30 mL), saturated NaHCO<sub>3</sub> (2 × 30 mL), and H<sub>2</sub>O (2 × 30 mL). The organic phase was dried over MgSO<sub>4</sub> for 12 h, filtered, and concentrated *in vacuo* (20 mbar, 30 °C) to afford **P2** as a white crystal powder (81 %); MALDI-TOF:  $M_w = 654$  Da; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta_H$  6.23-5.89 (*m*, 2H, CH=CH), 4.35-3.50 (*m*, 4H, OCH<sub>2</sub>CH<sub>2</sub> in PEG unit), 3.24-2.86 (*m*, 3H, CHCHCH<sub>2</sub>CH), 1.04-1.98 (*m*, 4H, CH<sub>2</sub>CHCH<sub>2</sub>) ppm.  $T_g$  was -30 °C as determined by DSC.

## 2. Planar template preparation

### 2.1 Allyl functionalization of Si wafer by deposition of allyl-PEI

A Si wafer (*ca.*  $1 \times 1$  cm) was added to a 7 mL vial containing 1 mL of allyl-PEI solution ( $1 \text{ mg}\cdot\text{mL}^{-1}$  in 0.5 M NaCl, passed through a  $0.45 \text{ }\mu\text{m}$  filter). The Si wafer was allowed to stand for 30 min at room temperature, removed and washed with water ( $1 \times 20$  mL), THF ( $2 \times 20$  mL) and DCM ( $3 \times 20$  mL). The obtained allylated Si wafer was then ready for immediate functionalization with Ru catalyst.

### 2.2 Surface immobilization of Ru catalyst initiating moieties on allylated Si wafer

To a dry 5 mL round bottom flask equipped with magnetic stirrer bar and 3-way stopcock was added the catalyst  $(\text{IMes})(\text{Cl}_2)(\text{C}_5\text{H}_5\text{N})_2\text{Ru}=\text{CHPh}$  **C1** (2.9 mg,  $4 \text{ }\mu\text{mol}$ ) and DCM (1 mL) under argon to yield a 4 mM stock solution. Separately, the allylated Si wafer (from method 2.1) was added to a 7 mL vial (dried and backpurged with argon). This was followed by the addition of 1 mL of the catalyst stock solution, via a degassed syringe, to the vial. The Si wafer and stock solution were allowed to stand at room temperature for 30 min. The catalyst-functionalized wafers were washed with DCM ( $2 \times 20$  mL) before being exposed to the macrocross-linker [P3HT-*co*-T2ONB] **P1**.

### 2.3. Film assembly via solid state $\text{CAP}_{\text{ROMP}}$

The catalyst-functionalised wafer (from method 2.2) was spin-coated with the macrocross-linker **P1** in  $\text{CHCl}_3$  ( $50 \text{ }\mu\text{L}$ ,  $20 \text{ mg}\cdot\text{mL}^{-1}$ , 2000 rpm, 33 s) and then annealed at  $150 \text{ }^\circ\text{C}$  under argon for a predetermined time. The  $\text{ssCAP}_{\text{ROMP}}$  reaction was stopped by soaking the wafer in DCM (5 mL) containing 2% v/v EVE for 1 h. The polymer-coated wafer was subsequently washed with and soaked in  $\text{CHCl}_3$  (1 mL) for 12 h to remove any non-cross-linked polymers, and dried *in vacuo* for analysis.

### 3. CAP multilayering

#### *ssCAP<sub>ROMP</sub> multilayering on planar substrates*

The previously assembled **P1** CAP film (i.e., L1) on Si wafer was added to a vial containing 1 mL of a solution of catalyst (IMes)(Cl<sub>2</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>Ru=CHPh **C1** (0.5 mM in DCM). After 30 min of soaking, the catalyst refunctionalized substrate was removed, washed with DCM (2 × 20 mL) and spin-coated with **P1** in CHCl<sub>3</sub> (50 μL, 10 mg·mL<sup>-1</sup>, 2000 rpm, 33 s). After annealing at 150 °C under argon for 24 h, the substrate was immersed in 2% v/v EVE in DCM (5 mL) for 1 h and then washed with CHCl<sub>3</sub> as previously described. After drying *in vacuo* the CAP films (i.e., L2) were analyzed and used for subsequent layering experiments (i.e., L3 to L5) via repetition of the above procedure.

#### 4. Supporting Figures

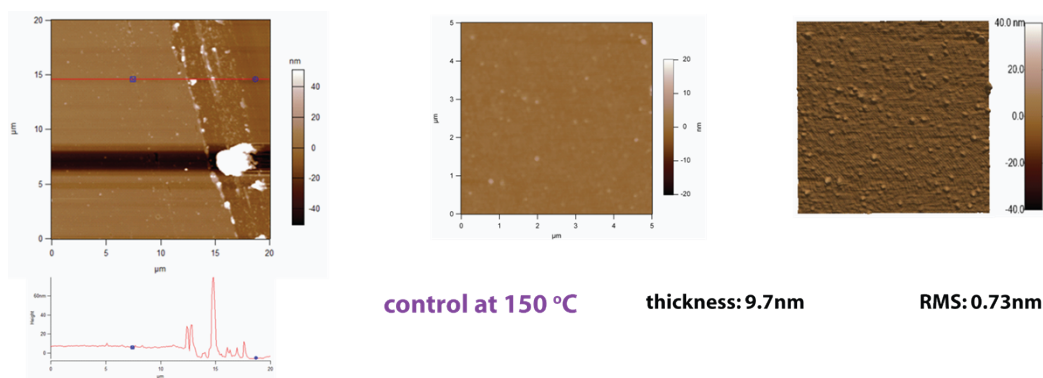


Figure S1. The z-profile of the scratched zone and (3D) height mode images of a control film made in the absence of C1 catalyst.

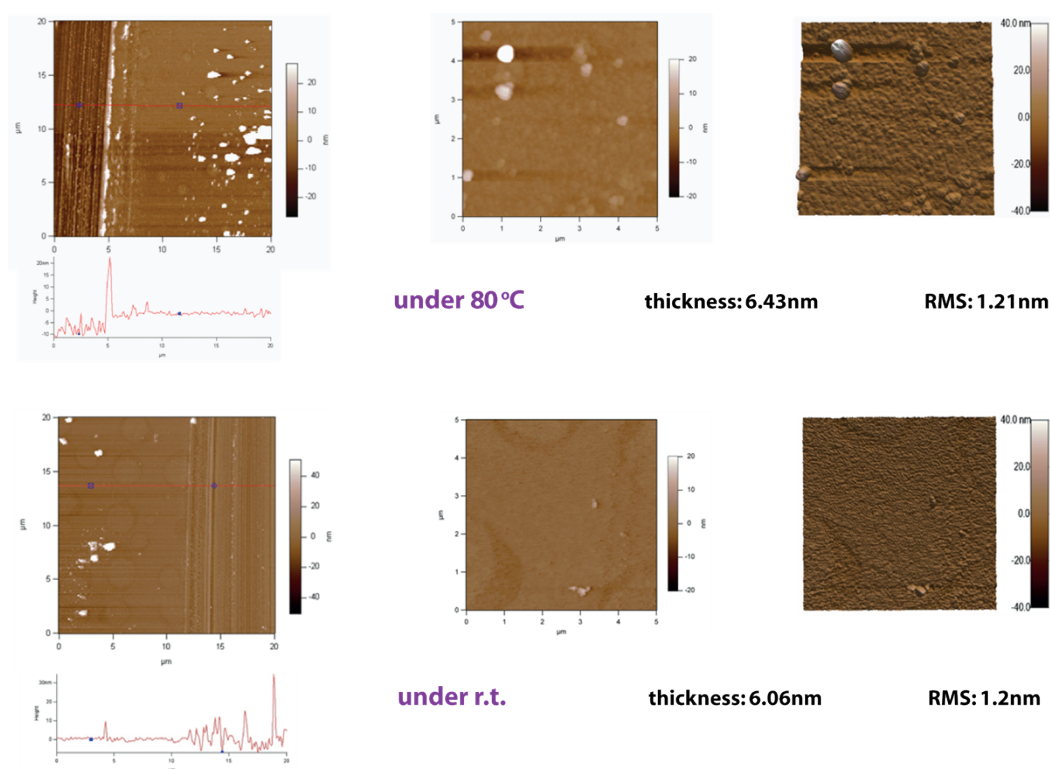


Figure S2. The z-profile of the scratched zones and (3D) height mode images of control films prepared at 80 °C and room temperature.

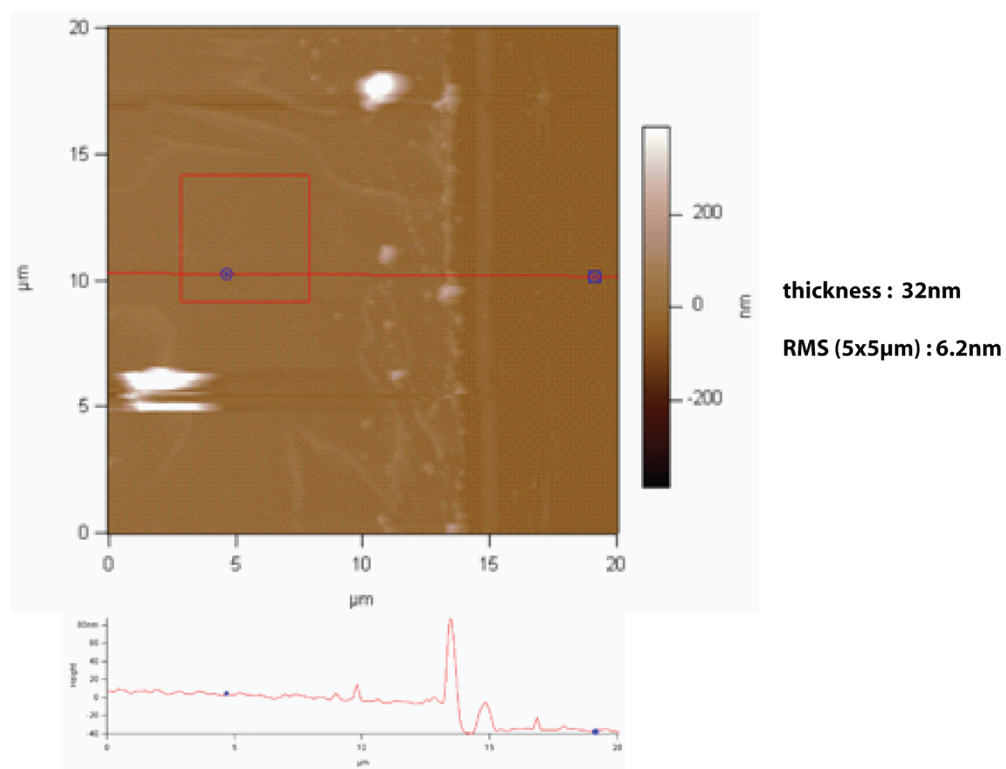


Figure S3. The z-profile of the scratched zone of a **P2** film made via ssCAP<sub>ROMP</sub>.

## References

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2. T.-A. Chen, X. Wu, R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233-244.