

Supporting Information

1. Experiment Section

1.1 General Method

Solvents were distilled using appropriate drying agents under nitrogen. Silicon wafers and ITO conductive glasses (<10 Ω /sq) were purchased from commercial sources. UV-vis spectra were performed using a PerkinElmer Lambda 35 UV-vis spectrophotometer. The ^1H NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Water-drop contact angles (WDCA) were evaluated using a commercial HARKE-SPCAX1 instrument. HPLC was conducted with a Waters 600 liquid chromatography. Cyclic voltammetry and Differential Pulse Voltammetry were performed with a Model 650A electrochemical system (CH Instruments Company, USA). The Pd content in the catalysts before and after the cross-coupling reactions was measured by performing inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an ICAP 6000 Series (Thermo Scientific), and the sample was treated as follows: the sample was broken down with nitrolysis, and then, the residual solid was dissolved with 2 M hydrochloric acid and transferred to a 10 mL volumetric flask to fix its quantity in water. An SPM-9500 J3 (Shimadzu Corporation, Japan) was used for AFM measurements in the air at ambient temperature. Cyclic Voltammetry (CV) curves were obtained using a CH 1650A. The experiments were performed in three electrode cells with 0.5 M HCl. The counter electrode was platinum; the reference electrode was Ag/AgCl/(0.1 M) KCl. Molecular weight was measured by GPC (Lab Tech). Si@PB4a2 ($n \cdot 3 \times 1 \text{ cm}^2$) and tetraoctylammonium bromide were dissolved in toluene (15 mL), to which a 10% HF aqueous solution (1 mL) was added. The mixture was vigorously stirred for 3 h. The cleaved polymer brush in THF was subjected to GPC measurements.

1.1.1 Procedure for Suzuki Reaction and Recycling Experiments

The Si@PB42a, base, and reactant were added to a 10 mL round-bottom flask with 4 mL solvent. The reaction was conducted in an oil bath at 80 °C or 100 °C for a specific duration. The catalysts were separated from the reaction mixture. For the recycling experiments, the reactions were conducted under the above conditions. After each run, the used catalyst was recovered from the reaction mixture and reused in sequential runs after washing with ethyl acetate, methyl alcohol, and water three times.

1.2 Synthesis and Characterization of Chiral Cyclopalladated Imines (R,p 4a2)

2a2, dark red solid. $[\alpha]_{\text{D}}^{20} = +2849^\circ$ (c 0.070, CH_2Cl_2). IR (KBr, ν , cm^{-1}): (-CH=N-) 3428. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (s, 1H, -CH=N-), 7.47 (d, $J = 7.2 \text{ MHz}$, 2H, PhH), 7.39 (t, $J = 7.6 \text{ MHz}$, 2H, PhH), 7.23 (t, $J = 7.2 \text{ MHz}$, 1H, PhH), 4.80 (s, 1H, C_5H_3), 4.31 (s, 1H, C_5H_3), 4.25 (s, 1H, C_5H_3), 4.18 (bs, 1H, OH), 4.13 (s, 1H, - CH_2Ph), 3.83 (dd, $J = 5.12 \text{ MHz}$, 40.64 MHz, 2H, - CH_2OH), 3.44–3.38 (m, 1H, =N-C*H),

2.95 (dd, $J = 3.28$ MHz, 13.44 MHz, 1H, $-CH_2Ph$). Yield: 48%.

3a2, saffron yellow solid. $[\alpha]_D^{20} = +1644$ °(c 0.093, CH_2Cl_2). IR (KBr, ν , cm^{-1}): ($-CH=N-$) 3381. 1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, $J = 8.04$, 1H, $-CH=N-$), 7.72–7.67 (m, 6H, $P(C_6H_5)_3$), 7.38–7.29 (m, 11H, $P(C_6H_5)_3+2PhH$), 7.23 (appt, $J = 7.40$ MHz, 2H, PhH), 7.12 (appt, $J = 7.28$ MHz, 1H, PhH), 4.70 (s, 1H, C_5H_3), 4.29 (s, 1H, C_5H_3), 3.96 (s, 1H, C_5H_3), 3.89–3.82 (m, 2H, $-CH_2OH$), 3.73 (s, 5H, C_5H_5), 3.30 (dd, $J = 6.92$ MHz, 13.76 MHz, 1H, $-CH_2Ph$), 3.26 (s, 1H, $=N-C^*H$), 3.00 (dd, $J = 7.96$ MHz, 13.72 MHz, 1H, $-CH_2Ph$). MS: 714 $[M-Cl+1]^{-1}$. Yield: 93%. The crystalline structure and data of 3a2 are presented in Figure S1 and Table S1, and Table S2.

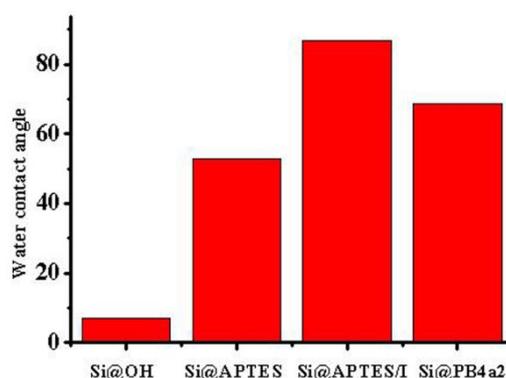


Figure S1 WDCAs at different preparation steps in the fabrication of the polymer brush (Si@PB4a2).

Table S1 Crystal data and structure refinement of complex 3a2.

Complexes	3a2
Formula	$C_{38}H_{35}ClFeNOPPd$
Fw	750.34
Temperature(K)	291(2)
wavelength(Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	12.6798(3)
b (Å)	9.49958(19)
c (Å)	14.3734(4)
a (deg)	90
b (deg)	107.312(3)
g (deg)	90
Volume(Å ³)	1652.89(7)
Z	2
D_c ($g \times cm^{-3}$)	1.508
$F(000)$	764
θ range for data collection(deg)	2.854–26.368
Reflections collected/unique	7868/5666

Data/restraints/parameters	5666/1/401
Goodness of fit on F^2	1.016
Final R_1^a , wR_2^b	0.0306, 0.0558

$$^a R_1 = \frac{1}{2} \frac{\sum (F_o - F_c)^2 / \sum F_o^2}{\sum F_o^2} \quad ^b wR_2 = \left[\frac{w \sum (F_o^2 - F_c^2)^2}{\sum F_o^2} \right]^{1/2}$$

Table S2 The selected bond lengths (Å) and angles (deg) of 3a2.

Complex 3a2					
Pd(1)-C(6)	1.991(5)	C(6)-Pd(1)-N(1)	80.63(18)	N(1)-Pd(1)-Cl(1)	93.58(12)
Pd(1)-N(1)	2.152(4)	C(6)-Pd(1)-P(1)	91.37(14)	P(1)-Pd(1)-Cl(1)	95.75(5)
Pd(1)-P(1)	2.244(2)	C(6)-Pd(1)-Cl(1)	168.3(1)	N(1)-Pd(1)-P(1)	168.33(12)
Pd(1)-Cl(1)	2.401(1)				

1.2.1 Crystal Structure Determination 1

X-ray diffraction data were collected with a Bruker APEXII CCD diffractometer at 298 ± 1 K using Mo-K α ray ($\lambda = 0.71073$ Å) for 3a2. All crystal structures were solved by direct methods with the Olex 2 crystallographic software package [1]. Crystal structures of 3a2 were refined by the full-matrix least-squares technique based on F^2 with the SHELXL-2014 crystallographic software package [2]. All atoms were refined anisotropically except hydrogen atoms. A summary of the crystallographic data and processing parameters is presented in Table S1. Table S2 shows the selected bond lengths and angles of 3a2.

1.2.2 Structural description of [Pd(L1)(PPh3)(Cl)] (1)

X-ray single-crystal diffraction revealed that complex 3a2 can crystallize in the monoclinic system, space group P21 as shown in Figure S1. The single-crystal X-ray analysis of complex 3a2 showed that the local coordination geometry for the four coordination Pd(II) centers is close to a tetrahedron geometry. Each Pd(II) ion binds four atoms, two atoms (N1, C6) from a chelating organic ligand L [Pd1-N1 = 2.152(3) Å and Pd1-C6 = 1.991(4) Å], and one phosphorus atom from triphenylphosphine ligand [Pd1-P1 = 2.2438 (10) Å]. The bond angles around the Pd(II) ion vary from 80.6314(14) to 168.33(9)°. The 1D chains are connected by the hydrogen bond O1-H1...Cl1 [H1...Cl1 = 2.44(6) Å, O1-H1...Cl1 = 167(6)°], leading to a 2D structure along the bc plane. The adjacent 2D structures align to build up a 3D structure through the formation of hydrogen bonds: C23-H23...C8 (H23...C8 = 2.918 Å), C18-H18...C2 (H18...C2 = 2.99 Å).

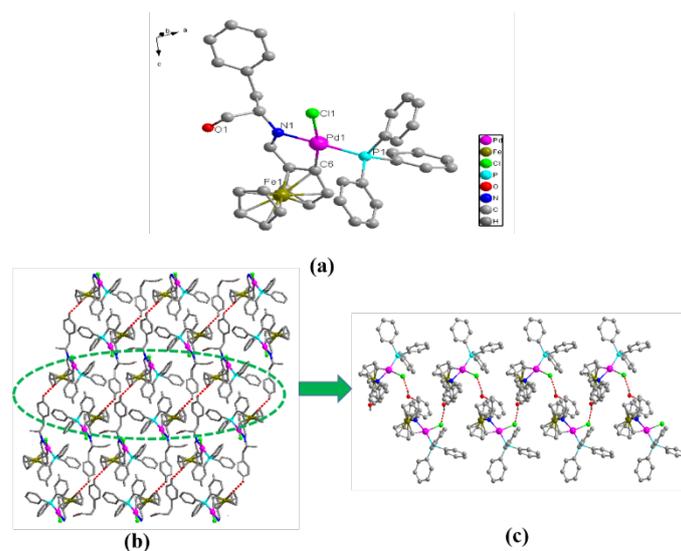


Figure S2 The coordination environment of the Pd(II) atom in 1. (b) The 3D structure of 3a2. (c) An infinite inorganic chain.

4a2, red solid. $[\alpha]_D^{20} = +1546$ (c 0.083, CH_2Cl_2). IR (KBr, ν , cm^{-1}): (-CH=N-) 3431, 2923, 2854. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 7.76$ MHz, 1H, -CH=N-), 7.81–7.76 (m, 6H, $\text{P}(\text{C}_6\text{H}_5)_3$), 7.45–7.37 (m, 11H, $\text{P}(\text{C}_6\text{H}_5)_3 + 2\text{PhH}$), 7.29 (appt, $J = 7.48$ MHz, 2H, PhH), 7.19 (appt, $J = 7.32$ MHz, ^1H , PhH), 6.49 (t, $J = 0.67$ MHz, 1H, -CH=CH₂), 6.19 (dd, $J = 10.4$ MHz, 17.32 MHz, 1H, -CH=CH₂), 5.86 (dd, $J = 0.68$ MHz, 10.36 MHz, 1H, -CH=CH₂), 4.64 (s, 1H, C_5H_3), 4.49 (dd, $J = 2.68$ MHz, 11.40 MHz, 1H, -CH₂Ph), 4.36 (s, 1H, C_5H_3), 4.03 (s, 1H, C_5H_3), 3.73 (s, 5H, C_5H_5), 3.65–3.58 (m, 2H, -CH₂OH), 3.30 (s, 1H, =N-C*H), 3.08 (dd, $J = 7.76$ MHz, 13.64 MHz, 1H, -CH₂Ph). MS: 768 $[\text{M}-\text{Cl}+1]^{-1}$. Yield: 86%.

1.3 Preparation of Cyclopalladated Ferrocenylimine Functionalized Polymer Brush (Si@PB4a2)

The details regarding the major steps of processing are as follows: (Si@PB4a2): Hydrophilic silicon treated by pirhana was functionalized with 3-aminopropyl triethoxysilane (2.1 mmol). Then, amino-functionalized wafers were immersed in a solution of 2-bromoisobutyryl bromide (3.3 mmol) in 25 mL of dry dichloromethane containing TEA (7.0 mmol) to react for 12 h, which resulted in the formation of initiator-functionalized wafers. Next, the initiator functionalized wafer was placed in a flask containing hydroxyethyl acrylamide (50 mmol), 2,2-bipyridine (1.0 mmol), CuCl (0.5 mmol), and 15 mL of a mixture (methanol/water: 4:1) and stirred for 4.5 h at room temperature in an atmosphere of nitrogen. Finally, the PHAM-grafted substrates were immersed in 40 mL of dried THF with N, N-carbonyl diimidazole (12 mmol), and a solution of cyclopalladated ferrocenylimines (0.001 g) in THF for 48 h to get Si@PB4a2.

1.4 Suzuki and Heck Coupling Reaction Catalyzed by 4a2 and Si@PB4a2

4a2, or Si@PB4a2 (2.5cm×1cm×0.1cm), a base, and a reactant were added to a 10 mL round-bottom flask with 4 mL solvent. The reaction was performed in an oil bath at 80 °C or 100 °C for a

certain duration. The catalysts were separated from the reaction mixture. For the recycling experiments, the reactions were conducted under the above conditions. After each run, the used catalyst was recovered from the reaction mixture and reused in sequential runs after washing with ethyl acetate, methyl alcohol, and water three times.

1.5 Recycling Experiments

For the recycling experiments, the reactions were conducted under the above conditions. After each run, the used catalyst was recovered from the reaction mixture by removing, and then reused in sequential runs after washing with ethyl acetate and methyl alcohol three times.

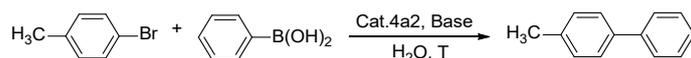
1.6 Hydrophilic Treatment

Silicon or ITO wafers were added to the mixture of concentrated nitric acid and concentrated sulfuric acid (v:v = 2:1) and boiled for 1–1.5 h. Then, the wafers were washed using deionized water, acetone, and chloroform. The ITO glasses were ultrasonic washed in acetone, ammonia, ethanol, and pure water, sequentially.

2. Optimal Conditions for the Suzuki and Heck Coupling Reactions Catalyzed By 4a2 and Si@Pb4a2

2.1 Optimal Conditions and Substrate Extension for the Suzuki Coupling Reaction Catalyzed by 4a2 in Homogeneous

Table S3 The effect of the base, temperature, and time on the Suzuki-Miyaura reaction conditions^a.

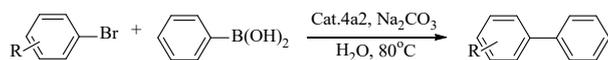


Entry	Base	Solvent	Temperature(°C)	T(h)	Yield ^b (%)
1	K ₃ PO ₄	H ₂ O	80	12	96
2	NaOH	H ₂ O	80	12	99
3	<i>t</i> -BuONa	H ₂ O	80	12	99
4	Na ₂ CO ₃	H ₂ O	80	12	99
5	NaHCO ₃	H ₂ O	80	12	98
6	NaOAc	H ₂ O	80	12	97
7	K ₂ CO ₃	H ₂ O	80	12	98
8	K ₂ HPO ₄ ·3H ₂ O	H ₂ O	80	12	54
9	NaH ₂ PO ₄ ·2H ₂ O	H ₂ O	80	12	52
10	Na ₂ CO ₃	H ₂ O	20	12	Trace
11	Na ₂ CO ₃	H ₂ O	40	12	21
12	Na ₂ CO ₃	H ₂ O	60	12	45
13	Na ₂ CO ₃	H ₂ O	80	6	29

14	Na ₂ CO ₃	H ₂ O	80	8	45
15	Na ₂ CO ₃	H ₂ O	80	10	54

^aReaction condition: 4-Bromotoluene 0.25 mmol, PhB(OH)₂ 0.30 mmol, base 0.30 mmol, catalyst 4a2 0.5 mmol%, n-Bu₄NBr 0.3 mmol, H₂O 2.0 mL. ^bYield determined by GC, based on the product.

Table S4 Suzuki coupling of aryl bromides with phenylboronic acid^a.

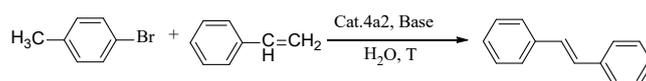


Entry	R	Product	Yield ^b (%)	TON
1	<i>p</i> -CF ₃		99	50
2	<i>p</i> -NO ₂		99	50
3	<i>m</i> -NO ₂		99	50
4	<i>o</i> -NO ₂		96	48
5	<i>p</i> -CN		99	50
6	<i>o</i> -CN		94	47
7	<i>p</i> -NH ₂		82	41
8	<i>m</i> -OCH ₃		89	45
9	<i>o</i> -OCH ₃		85	43
10	<i>p</i> -OCH ₃		95	47

^aReaction condition: Aryl bromide 0.25 mmol, PhB(OH)₂ 0.30 mmol, base 0.30 mmol, catalyst 4a2 (0.5 mmol%), n-Bu₄NBr (0.3 mmol), H₂O 2.0 mL, 80 °C, 12 h. ^bYield determined by GC, based on the product.

2.2 Optimal Conditions for Substrate Extension for the Heck Coupling Reaction Catalyzed By 4a2 in Homogeneous

Table S5 The effect of the base, temperature, and reaction time on Heck coupling^a.

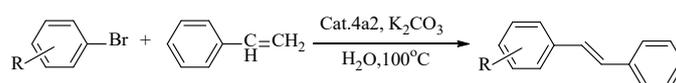


Entry	Base	Solvent	Temperature(°C)	T(h)	Yield ^b (%)
1	K ₃ PO ₄	H ₂ O	100	12	88
2	NaOH	H ₂ O	100	12	99
3	<i>t</i> -BuONa	H ₂ O	100	12	99
4	Na ₂ CO ₃	H ₂ O	100	12	98

5	NaHCO ₃	H ₂ O	100	12	95
6	NaOAc	H ₂ O	100	12	61
7	K ₂ CO ₃	H ₂ O	100	12	99
8	K ₂ HPO ₄ ·3H ₂ O	H ₂ O	100	12	87
9	NaH ₂ PO ₄ ·2H ₂ O	H ₂ O	100	12	51
10	K ₂ CO ₃	H ₂ O	20	12	Trace
11	K ₂ CO ₃	H ₂ O	40	12	25
12	K ₂ CO ₃	H ₂ O	60	12	49
13	K ₂ CO ₃	H ₂ O	80	12	76
14	K ₂ CO ₃	H ₂ O	100	6	29
15	K ₂ CO ₃	H ₂ O	100	8	45
16	K ₂ CO ₃	H ₂ O	100	10	75

^a Reaction condition: PhBr 0.25 mmol, styrene 0.75 mmol, base 0.3 mmol, catalyst 4a2 0.5 mmol%, n-Bu₄NBr 0.3 mmol, H₂O 2.0 mL. ^bYield determined by GC, based on the product.

Table S6 Heck coupling of aryl halides with styrene ^a.

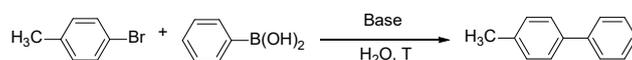


Entry	R	Product	Yield ^b (%)	TON
1	<i>p</i> -CF ₃		99	50
2	<i>p</i> -NO ₂		99	50
3	<i>m</i> -NO ₂		99	50
4	<i>o</i> -NO ₂		36	18
5	<i>p</i> -CN		99	50
6	<i>o</i> -CN		26	13
7	<i>p</i> -NH ₂		47	24
8	<i>m</i> -CH ₃ O		33	17
9	<i>o</i> -CH ₃ O		11	5.5

^a Reaction condition: PhBr 0.25 mmol, styrene 0.75 mmol, K₂CO₃ 0.3 mmol, catalyst 4a2 0.5 mmol%, n-Bu₄NBr 0.3 mmol, H₂O 2.0 mL, 100 °C; reaction time: 12 h. ^bYield determined by GC, based on the product.

2.3 Optimal Conditions and Substrate Extension for the Suzuki Coupling Reaction Catalyzed by *Si@Pb4a2* in Heterogeneous

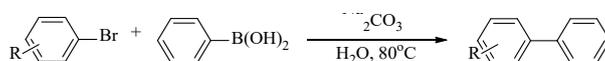
Table S7 The effect of the base, temperature, and reaction time on the Suzuki-Miyaura reaction conditions ^a.



Entry	Base	Solvent	Temperature(°C)	T(h)	Yield ^b (%)
1	K ₃ PO ₄	H ₂ O	80	12	89
2	NaOH	H ₂ O	80	12	99
3	<i>t</i> -BuONa	H ₂ O	80	12	99
4	Na ₂ CO ₃	H ₂ O	80	12	92
5	NaHCO ₃	H ₂ O	80	12	90
6	NaOAc	H ₂ O	80	12	96
7	K ₂ CO ₃	H ₂ O	80	12	99
8	K ₂ HPO ₄ ·3H ₂ O	H ₂ O	80	12	49
9	NaH ₂ PO ₄ ·2H ₂ O	H ₂ O	80	12	48
10	K ₂ CO ₃	H ₂ O	20	12	9
11	K ₂ CO ₃	H ₂ O	40	12	11
12	K ₂ CO ₃	H ₂ O	60	12	67
13	K ₂ CO ₃	H ₂ O	80	6	31
14	K ₂ CO ₃	H ₂ O	80	8	56
15	K ₂ CO ₃	H ₂ O	80	10	89

^aReaction condition: 4-Bromotoluene 0.25 mmol, PhB(OH)₂ 0.30 mmol, **Si@PB4a2** (8.38 × 10⁻⁶ mmol/cm²), base 0.30 mmol, *n*-Bu₄NBr 0.3 mmol, H₂O 2.0 mL; reaction time: 12 h. ^bYield determined by GC, based on the product.

Table S8 Suzuki coupling of aryl bromides with phenylboronic acid^a.



Entry	R	Product	Yield ^b (%)	TON
1	<i>p</i> -CF ₃		99	11933
2	<i>p</i> -NO ₂		99	11933
3	<i>m</i> -NO ₂		96	11456
4	<i>o</i> -NO ₂		92	10978
5	<i>p</i> -CN		99	11933
6	<i>o</i> -CN		90	10970

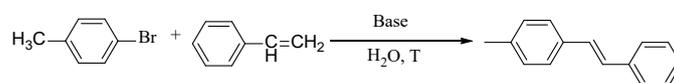
7	<i>p</i> -NH ₂		82	9785
8	<i>m</i> -OCH ₃		79	9427
9	<i>o</i> -OCH ₃		71	8472
10	<i>p</i> -OCH ₃		88	10352

^aReaction condition: Aryl compounds 0.25 mmol, PhB(OH)₂ 0.30 mmol, base 0.30 mmol, **Si@PB4a2** (8.38×10^{-6} mmol/cm²), n-Bu₄NBr 0.3 mmol, H₂O 2.0 mL, 80 °C; reaction time: 12 h.

^bYield determined by GC, based on the product.

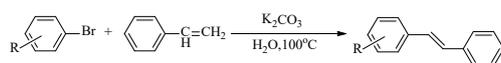
2.4 Optimal Conditions and Substrate Extension for the Heck Coupling Reaction Catalyzed by **Si@PB4a2** in Heterogeneous

Table S9 The effect of the base, temperature, and reaction time on Heck coupling ^a.



Entry	Base	Solvent	Temperature(°C)	T(h)	Yield ^b (%)
1	K ₃ PO ₄	H ₂ O	100	12	92
2	NaOH	H ₂ O	100	12	99
3	<i>t</i> -BuONa	H ₂ O	100	12	99
4	Na ₂ CO ₃	H ₂ O	100	12	68
5	NaHCO ₃	H ₂ O	100	12	66
6	NaOAc	H ₂ O	100	12	76
7	K ₂ CO ₃	H ₂ O	100	12	99
8	K ₂ HPO ₄ ·3H ₂ O	H ₂ O	100	12	65
9	NaH ₂ PO ₄ ·2H ₂ O	H ₂ O	100	12	44
10	K ₂ CO ₃	H ₂ O	20	12	Trace
11	K ₂ CO ₃	H ₂ O	40	12	21
12	K ₂ CO ₃	H ₂ O	60	12	69
13	K ₂ CO ₃	H ₂ O	80	12	82
14	K ₂ CO ₃	H ₂ O	100	6	23
15	K ₂ CO ₃	H ₂ O	100	8	50
16	K ₂ CO ₃	H ₂ O	100	10	89

^aReaction condition: PhBr 0.25 mmol, styrene 0.75 mmol, base 0.3 mmol, **Si@PB4a2** (8.38×10^{-6} mmol/cm²), n-Bu₄NBr 0.3 mmol, H₂O 2.0 mL. ^bYield determined by GC, based on the product.

Table S10 Heck coupling of aryl halides with styrene ^a.

Entry	R	Product	Yield ^b (%)	N
1	<i>p</i> -CF ₃		99	1933
2	<i>p</i> -NO ₂		99	1933
3	<i>m</i> -NO ₂		90	0740
4	<i>o</i> -NO ₂		88	0533
5	<i>p</i> -CN		99	1933
6	<i>o</i> -CN		32	582
7	<i>p</i> -NH ₂		62	398
8	<i>m</i> -CH ₃ O		60	395
9	<i>o</i> -CH ₃ O		16	1909

^a Reaction condition: PhBr 0.25 mmol, styrene 0.75 mmol, K₂CO₃ 0.3 mmol, catalyst **Si@PB4a2** (8.38×10^{-6} mmol/cm²), n-Bu₄NBr 0.3 mmol, H₂O 2.0 mL, 100 °C; reaction time: 12 h. ^b Yield determined by GC, based on the product.

3. Figures

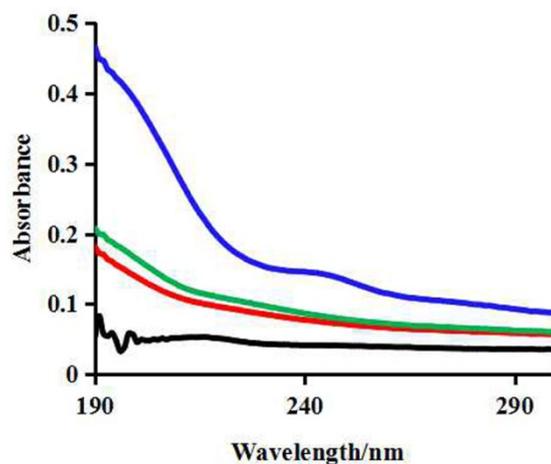


Figure S3 UV-vis absorption spectra for the preparation of **Si@PB4a2**. Si@OH, black line; Si@APTES, red line; Si@APTES/I, green line; **Si@PB4a2**, blue line.

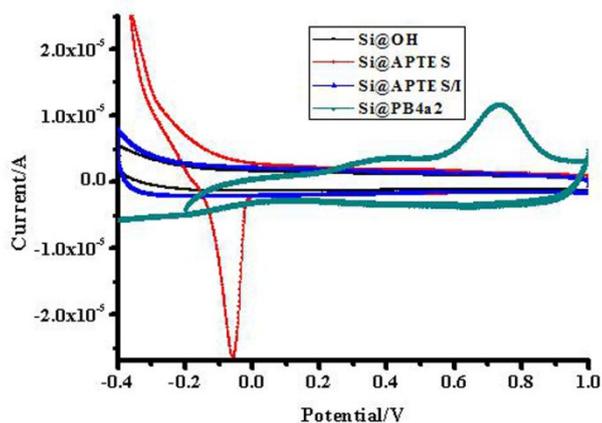


Figure S4 Cyclic voltammograms of polymer brush. Black line: ITO@OH; Red line: ITO@APTES; Blue line: ITO@APTES/I; Green line: ITO@ PB 4a2.

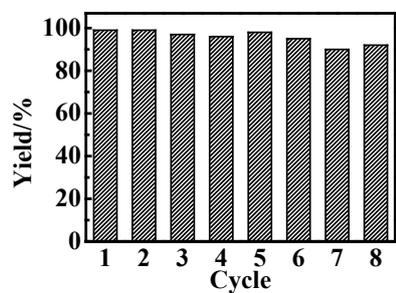


Figure S5 Recycling of the Si@ PB 4a2 polymer brush in the Suzuki coupling reaction.

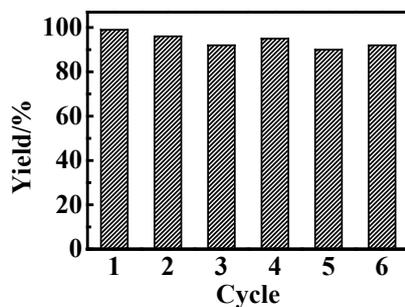


Figure S6 Recycling of the Si@PB 4a2 polymer brush in the Heck reaction.