

The Recyclable Cyclopalladated Ferrocenyimine Self-assembly Film and Its Mechanism Investigation of Heterogeneous Catalysis

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1. Experimental Section

1.1. General

All solvents were obtained from commercial sources and dried and freshly distilled prior to use. The cyclopalladated ferrocenyimine was prepared according to the published procedures [1]. All other chemicals were used as purchased. The catalyst films were performed on commercially available silicon, quartz slides (usually cut into 10 mm×10 mm or 30 mm×10 mm) and Round-bottomed flask (5 mL), which were hydrophilic treatment by piranha solution (H₂SO₄/H₂O₂ (7:3; v:v)) for 1.5 h at 90 °C to remove any organic residues and to create silanol groups on the surfaces.

UV-vis spectra were recorded with a Lambda 35 UV-vis spectrophotometer (Perkin Elmer Inc. USA). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK α radiation. The base pressure was about 3×10⁻⁹ mbar. The binding energies were referenced to the C1s line at 284.8eV from adventitious carbon. Scanning electron microscope images were taken by JSM-6700 (10.0kV). A SPM-9500 J3 (Shimadzu Corporation, Japan) was employed for AFM measurements in air at ambient temperature. Atomic Absorption Spectroscopy (AAS) analysis was obtained by Z-8000 polarized Zeeman atomic absorption spectrophotometer (Hitachi Corporation, Japan). Low-angle X-ray diffraction data were obtained with an X' Pert PRO X-ray diffractometer from PANalytical using Copper target, continuously scanning as 40 mA tube current, 40 kV tube voltage. Cyclic Voltammetry (CV) curves were obtained by CH 1650A, ITO glasses electrode (30×10×1 mm) was used as working electrode. The reference electrode was a saturated calomel electrode (SCE), while the counter electrode was a Pt wire. The electrolytic medium was H₂O (Millipore Q-grade, 18.2 MU cm) containing 0.1 M HCl. All the Suzuki reaction was accomplished without the protection of inert gas. HPLC was conducted on a Waters 600 liquid chromatography. The HPLC conditions were a Zorbax eclipse Xdb C18 column (150 4.6 mm, 5 μ m) with, a flow rate 1 mL/min. The HPLC conditions were a Kromasil C18 column (150×4.6 mm, 5 μ m).

2. The synthesis of cyclopalladated ferrocenyimines SAM-films (Si- CDI-Pd)

The freshly hydroxyterminated silicon or quartz surfaces were placed in a solution of 0.5 mL of 3-aminopropyl triethoxysilane (2.1 mmol) in 30 mL of dry toluene. After being treated at 80 °C for 24 h, and then washed successively with toluene, methanol, water, and acetone, dried in a nitrogen stream. The amino-functionalized substrates were immersed in 40 mL of dried THF, containing 1.95 g of CDI, for 48 h at room temperature to give rise to the CDI surfaces. then resulting substrates were rinsed with copious amounts of THF, deionized water, acetone, and subsequently introduced into 15 mL dried THF containing 0.001 g of catalyst for 48 h at room

temperature to produce the cyclopalladated ferrocenylimines catalyst SAM-films. After the reaction, the catalyst-grafted substrates were washed thoroughly with dichloromethane and acetone, prior to being dried in a nitrogen stream.

1.3. General procedure for the Suzuki cross-coupling reaction of aryl halide with phenyl boronic acid

Aryl halide (0.125 mmol), phenylboronic acid (0.15 mmol), K_2CO_3 (0.15 mmol) and $n-Bu_4NBr$ (0.15 mmol) were combined with 3 mL water in a small round-bottom flask used for “homogeneous” and “heterogeneous” runs. The reaction mixture was stirred at 80 °C for 12 h, then, the mixture was acidified, and the product was extracted by ethyl ether for three times. The combined organic phase was dried with $MgSO_4$, filtered, and solvent was removed on a rotary evaporator. Crude product was transferred into a 10 mL volumetric flask to fix its quantity in ethyl acetate. The yields were determined by high performance liquid chromatography (HPLC), based on the peak area ratio between bromobenzene and the product. The HPLC conditions were a Kromasil C18 column (150×4.6 mm, 5 mm) with methanol/acetonitrile as the mobile phase e, a flow rate 0.8 mL/min, column temperature 25 °C, UV-detection wavelength 272 nm (phenylboronic acid) and the sample size 20 mL.

1.4 Atomic emission Spectroscopy analysis

The amounts of cyclopalladated ferrocenylimines immobilized on solid substrates were measured by inductively coupled plasma atomic emission spectroscopy (ICPAES) (ICAP 6000 Series, Thermo SCIENTIFIC). The sample treatments were as follows: **Si-CDI-Pd** (quartz plate or round-bottomed flask) were boiled in concentrated nitric acid, and then, residual solid was dissolved with 2 M hydrochloric acid and transferred into a 10 mL volumetric flask to fix its quantity in water.

1.5 General procedure for controlled trials

First, **Si-CDI-Pd** substrates was put into round-bottom flask with Aryl halide (0.125 mmol), phenylboronic acid (0.15 mmol), K_2CO_3 (0.15 mmol), $n-Bu_4NBr$ (0.15 mmol) and 3 mL water. Then it was taken out from the reaction mixture after three hours, 38 % yields of product was detected. No more products could be obtained if the reaction continued to 24 hours without **Si-CDI-Pd**. However, when the catalyst substrate (**Si-CDI-Pd**) was put back into a new reaction solution, a yield of 93 % products could be obtained after 12 hours again.

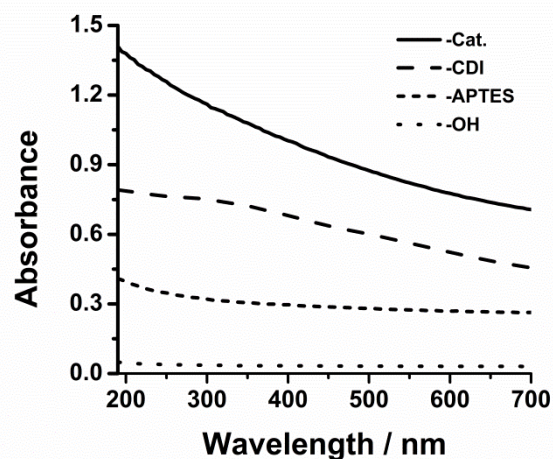


Figure S1. UV-vis absorption spectra of modified quartz plates. -OH (Hydrophilic quartz substrate), -APTES (quartz substrate treated by 3-aminopropyl triethoxysilane), -CDI (quartz substrate modified by carbonyldiimidazole), -Cat. (quartz substrate linked by cyclopalladated ferrocenyliimines)

Table S1. Summary of the binding energies observed of modified silicon wafer surfaces.

	Binding energies (eV)									
	Si 2p		Cl 2p		C 1s		Pd 3d		Fe 2p	
	bulk	oxide			pk 1	pk 2	3d _{5/2}	3d _{3/2}		
silanization	99.1	102.6			284.8	289.1	399.1			
CDI addition	99.1	102.4			284.8		399.4			
catalyst attachment	98.4	102.0	198.0		284.9	289.4	399.5	337.9	343.2	708.4

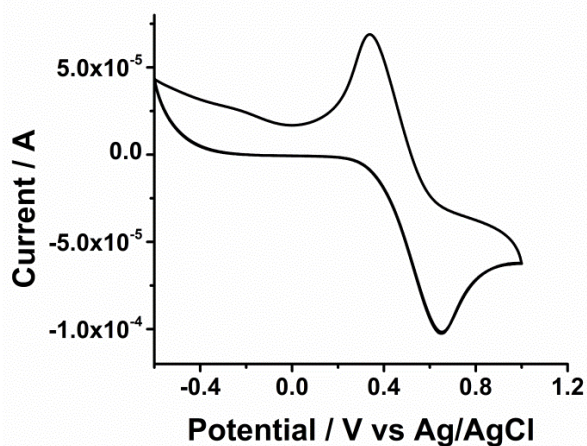


Figure S2. Cyclic voltammograms of cyclopalladated ferrocenyliimines in THF solution at scan rate of 10 mV/s.

Table S2. Summary of the cyclic voltammograms observed.

	E _{pa} (mV)	E _{pc} (mV)	ΔE _p (mV)
catalysts in solution	653	338	315
Si-CDI-Pd	519	299	220

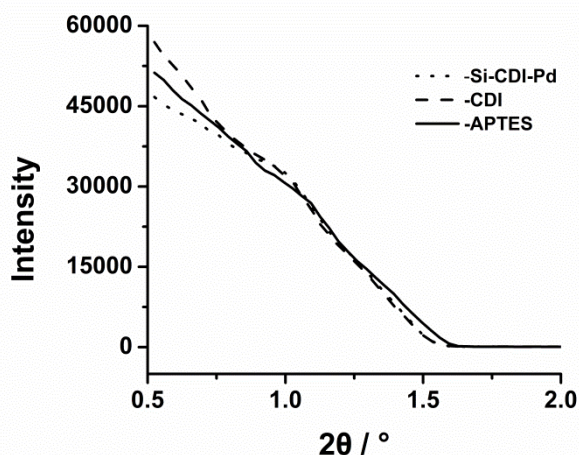


Figure S3. The LAXRD patterns of modified silicon wafer surfaces. -APTES (treated by 3-aminopropyl triethoxysilane), -CDI (silicon wafer modified by carbonyldiimidazole), -Si-CDI-Pd (silicon wafer linked by cyclopalladated ferrocenylimines).

Table S3. Investigation of the Suzuki-Miyaura reaction conditions in water. ^a

Entry	Base	Solvent	T (°C)	Yield ^b (%)
1	Na ₂ CO ₃	H ₂ O	90	82
2	K ₃ PO ₄	H ₂ O	90	70
3	KOH	H ₂ O	90	89
4	K ₂ CO ₃	H ₂ O	90	97
5	Et ₃ N	H ₂ O	90	85
6	NaHCO ₃	H ₂ O	90	96
7	NaOAc	H ₂ O	90	67
8	K ₃ PO ₄ ·7H ₂ O	H ₂ O	90	96
9	K ₂ CO ₃	H ₂ O	30	45
10	K ₂ CO ₃	H ₂ O	70	78
11	K ₂ CO ₃	H ₂ O	80	99

[a] Reaction condition: 4-bromotoluene 0.125 mmol, PhB(OH)₂ 0.15 mmol, K₂CO₃ 0.15 mmol, n-Bu₄NBr(TBAB) 0.15 mmol, H₂O 3 mL, T, 12 h. Quartz plate (30 mm×10 mm×1 mm). [b] Yields determined by HPLC, based on the products.

Table S4. ICP-AES Analysis of the amount of Pd grafted onto round bottomed flasks during recycling experiments in the coupling of 4-bromotoluene with arylboronic acid.

	No reaction	2th	4th	6th	8th
n_{Pd}(mmol)	7.57×10 ⁻⁶	6.93×10 ⁻⁶	6.90×10 ⁻⁶	6.52×10 ⁻⁶	5.91×10 ⁻⁶

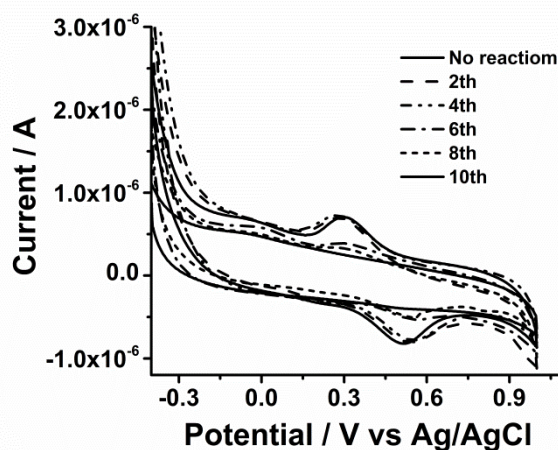


Figure S4. Cyclic voltammograms of Si-CDI-Pd grafted on ITO glass in recycling experiments in 1 M HCl solution at scan rate of 10 mV/s.

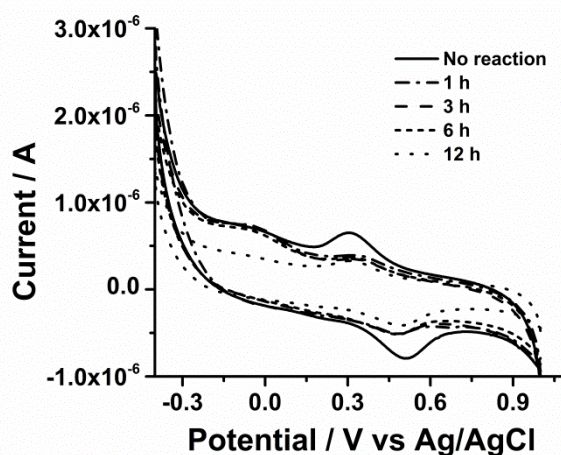


Figure S5. Cyclic voltammograms of Si-CDI-Pd grafted on ITO glasses in Suzuki-Miyaura reaction at different reaction time in 1 M HCl solution at scan rate of 10 mV/s

Table S5. Summary of the Binding Energies of Pd3d, B1s and Br3d of Si-CDI-Pd in Suzuki-Miyaura reaction at 0 h, 0.5 h, 1 h, 6 h and 12 h.

	Binding Energy (eV)			
	Pd3d _{3/2}	Pd3d _{5/2}	B1s	Br3d
0 h	343.2	337.9		
0.5 h	343.3	341.1	338.1	335.8
1 h	342.1		336.8	191.7
6 h	343.2	340.5	337.6	335.2
12 h	343.1		337.8	192.5

Notes and references

1 a) Mu, B, T. S. Li,* W. J. Xu, G. L.Zeng, P. P. Liu,Y. J. Wu*, *Tetrahedron*, **2007**, *63*, 11475-11488. b) Y.J. Wu, F. Yang, J.L. Zhang, X.L. Cui, J.F. Gong, M.P. Song, T.S. Li, *Chinese Science Bulletin* **2010**, *55*, 2784-2793.

