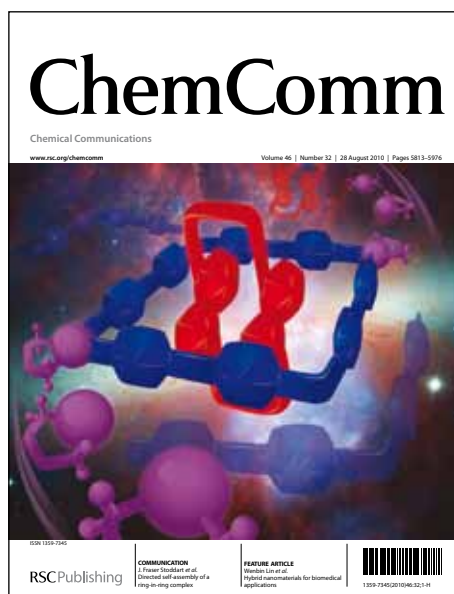


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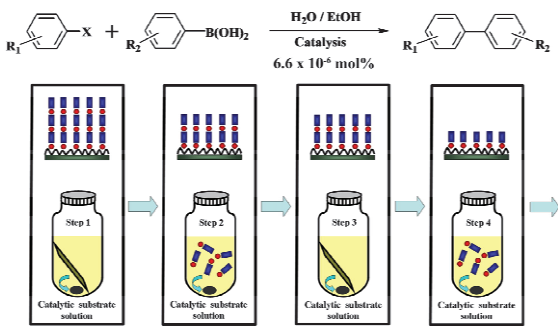
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Graphical abstract

Assembly of a Multilayer Film and Catalytic Application in Suzuki Cross-coupling Reaction Based on Synergistic Effect of a Conjugated Organometallic Pyridyl $\text{Pt}(\text{C}\equiv\text{C})_2$ Moieties with Palladium

Xing Li, Xiuhua Zhao, Jie Zhang and Yayun Zhao



A multilayer film loaded on the slide was capable of gradually discharging trace amount Pd-catalysts (ppm) to promote the Suzuki cross-coupling reactions with high efficiency in $\text{H}_2\text{O}/\text{EtOH}$ solution.

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ARTICLE TYPE

Assembly of a Multilayer Film and Catalytic Application in Suzuki Cross-coupling Reaction Based on Synergistic Effect of a Conjugated Organometallic Pyridyl Pt(C≡C)₂ Moieties with Palladium

Xing Li,^{*a} Xiuhua Zhao,^a Jie Zhang^b and Yayun Zhao^a⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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A multilayer film (Pd²⁺/1)_n was prepared with Pd(II) ions and platinum compound *trans*-[Pt(PPh₃)₂(C≡CPy)₂] (**1**) through layer-by-layer self-assembly method. The film loaded on the quartz slide could be capable of discharging high catalytic active Pd species to promote the C-C coupling reaction, with extraordinarily low Pd-loading (6.6 × 10⁻⁶ mol%) and high catalytic efficiency in H₂O / EtOH solution.

The assembly of ordered architectures by using the linear organometallic motifs to modify the solid surfaces, was much less explored in the previous studies.¹ Fortunately, The transition metal coordination chemistry provides new opportunities for preparing the multilayer film, in which metal particles are orderly deposited on the surfaces of the films, and can gradually release high catalytic active nanoparticles in the reactions.²⁻⁴ It has been documented that rigid pyridyl Pt-acetylide blocks may be useful potential candidates for assembly of the functionalized multilayer film.⁵

As part of our interest in the preparation of organometallic compounds with unsaturated groups, we have carried out a study of the pyridyl-acetylene platinum featuring large conjugated electronic groups, which can offer both alkyne-π system and pyridine nitrogen atoms readily bonding to metal centers and should be useful in the assembly of metal-ligand multilayer films.

For instance, Pd-organic ligand films were successfully assembled by alternating adsorption organic ligands and Pd(II) ions onto solid slides,⁶ and Pd-pyridyl complexes were loaded within the multilayer films, which as catalysts in the coupling reaction showed considerable high catalytic activity.^{4,7,8}

Here, we prepared a bridging organometallic ligand *trans*-[Pt(PPh₃)₂(C≡CPy)₂] (**1**, py = pyridyl), and characterized by IR, UV-vis, NMR, XPS, and single X-ray diffraction (ESI). The compound above was acted as a linear motif to assemble

(Pd²⁺/1)_n multilayer films from **1** and PdCl₂ by layer-by-layer technique, in which pyridine N atoms can bond palladium centers well. The multilayer film as a catalyst reservoir was performed the application to the Suzuki coupling reaction. To the best of our knowledge, this is rare case so far that the pyridyl-acetylene platinum compound as the organometallic ligand is employed to prepare the multilayer film loaded on the quartz slides for the catalytic reaction.

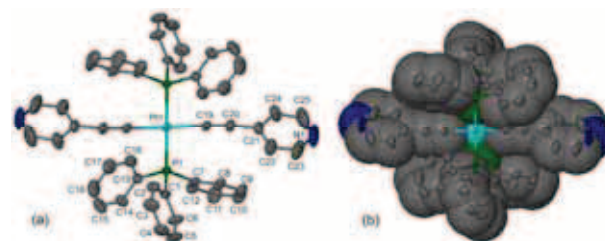


Fig. 1 (a) A plot of *trans*-[Pt(C≡CPy)₂(PPh₃)₂] (**1**), the hydrogen atoms are removed for clarity; (b) its space-filling mode.

Single X-ray diffraction analysis showed that **1** is a mononuclear (Fig. 1). The Pt(II) ion is a four coordinated geometry comprised *trans*-oriented C₂P₂ donors from σ-coordinated acetylides and PPh₃ ligands. The Py-C≡C-Pt-C≡C-Py array is quasi-linear in **1**. Triple bond is confirmed by the feature peak of 2110 cm⁻¹ (ν(C≡C)) in IR spectra with the bond distance being 1.195(11) Å (ESI). All crystallized data with bond lengths and angles are listed in table S1 and Table S2. The absorption spectra of **1** at 220 nm due to the n-π* transitions, and the broad absorption band 300–400 nm is tentatively attributed to the π-π* transitions (Fig. S4), probably along with some d(Pt)→π* MLCT (Metal-to-ligand charge transfer) character.^{9,10}

The growth process of the film was monitored with UV-vis spectroscopy. As shown in Fig. 2, the maximum absorption peak centered at 350 nm for the film PEI-(Pd²⁺/1)_n (n = 1–10, PEI = polyethylenimine) was consistent with one of **1** with no position change of the absorption peak during the film assembly process, but Pd²⁺ ions adsorption resulted in the absorbance increase upon adding deposition layers. The absorbance increases was close to linear with R² = 0.9824 between the absorption at λ_{max} = 350 nm and the number of bilayers, suggested that **1** was incorporated in the films PEI-(Pd²⁺/1)_n for the first ten layers. Thus, metal-pyridyl coordination interactions were responsible for the LbL deposition

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† Electronic Supplementary Information (ESI) available: IR, UV-vis, NMR, XPS, preparation of the materials, crystallographic data and catalytic experiments. See DOI: 10.1039/b000000x/

between metal ions and **1** by using its pyridyl groups. The desorption experiments were also prove that the assembly of the multilayer film was in layer-by-layer manner, monitored by UV-vis spectra (Fig.S5). The amount of Pd in multilayer film PEI-(Pd²⁺/1)₁₀ is 7.0 μg (6.6 × 10⁻⁶ mol%), determined by UV-vis spectra and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) techniques (Details, see ESI). The XPS results confirmed the presence of all the proleptic elements in the films (Fig. 3, Fig. S6),^{11,12} in the other words, PdCl₂/1 components were deposited on the substrates.

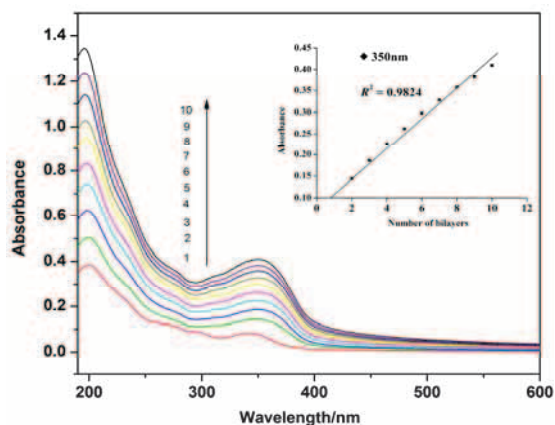


Fig. 2 UV-vis spectra of the multilayer film of PEI-(Pd²⁺/1)₁₀.

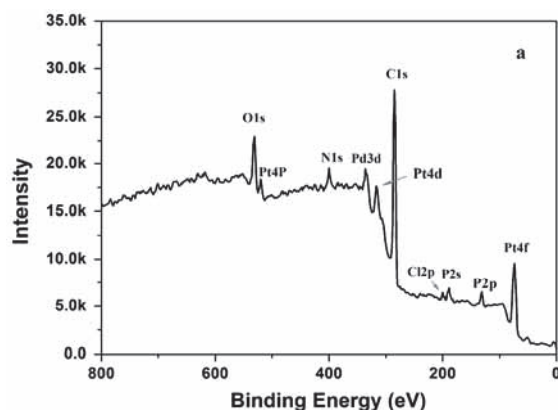


Fig. 3 XPS view of the film (PdCl₂/1)₁₀ deposited on the single crystal silicon substrate. (a) Survey. (b) Pd_{3d}; (c) Pt_{4f} in ESI.

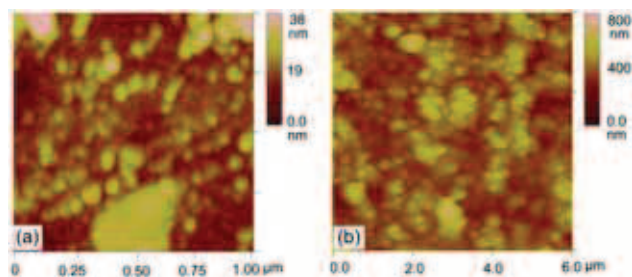


Fig. 4 AFM height images of the films. (a) PEI-(Pd²⁺/1)₅ (Rrms = 5.667 nm). (b) PEI-(Pd²⁺/1)₁₀ (Rrms = 72.945 nm).

Atomic force microscopy images of the multilayer films was shown in Fig. 4. The height images of PEI-(Pd²⁺/1)_n showed that aggregated nano-particulates were compactly distributed on the quartz slides with the vague boundaries

among particles. As shown in Fig. 4a, some larger aggregated particles as islets were unevenly distributed on the surface of the film PEI-(Pd²⁺/1)₅ with root-mean-square roughness being 5.677 nm. Upon increasing the film number, more particle aggregates were observed and the island-shaped nanostructures were dispensed on the film surface with the RMS roughness 72.945 nm for ten layer film PEI-(Pd²⁺/1)₁₀ (scan area 6.0 × 6.0 μm²). (Fig. 4b).

The Suzuki cross-coupling reactions were carried out by using the slide coated with PEI-(Pd²⁺/1)₁₀ films as catalysts, in which the coated slides were immersed into the reaction mixtures. After the reaction finished, the desired products were separated by extraction and purification. As shown in Table 1, the *para*-substituted aryl bromides with electron-withdrawing groups (e.g., CN, CF₃) gave the relevant biaryls in high yields at 50 °C for 4h (Table 1, entry 2 and 3). The electron-donating group (e.g., 4-MeO) of aryl bromide also offered the high yield in the same reaction condition (Table 1, entry 4). However, the *ortho*-substituent (2-MeO) gave rise to the low yield of the biaryl products due to the steric hindrance effect in the reaction (Table 1, entry 5), even though longer reaction time and higher temperature were executed in the reaction system, it was very difficult to reach considerably high yield (Table 1, entry 6), comparing with one of entry 4 in table 1. The *para*-substituted arylboronic acids with electron-donating substituents (e.g., Me, 4-MeO) favored the coupling reactions (Table 1, entry 7 and 8). Even for the *ortho*-substituted arylboronic acid (e.g., 2-MeO), it also gave high yield (Table 1, entry 9), in which the steric hindrance little affected the result of the reactions (Details in Table S3).

Table 1 Suzuki cross-coupling reactions of aryl halides with arylboronic acids using (Pd²⁺/1)₁₀ films as catalysts

$R_1\text{-C}_6\text{H}_4\text{-X} + R_2\text{-C}_6\text{H}_4\text{-B(OH)}_2 \xrightarrow[\text{Catalyst, } 6.6 \times 10^{-6} \text{ mol\%}]{\text{H}_2\text{O/EtOH, K}_2\text{CO}_3} R_1\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-R}_2$						
Entry	R ₁	R ₂	X	T/°C, hour	Yield	TON × 10 ⁴
1	H	H	Br	50, 4h	98	1.49
2	4-CN	H	Br	50, 4h	99	1.50
3	4-CF ₃	H	Br	50, 4h	98	1.49
4	4-MeO	H	Br	50, 4h	95	1.44
5	2-MeO	H	Br	50, 4h	38	0.58
6	2-MeO	H	Br	100, 24h	86	1.31
7	H	4-Me	Br	50, 4h	92	1.40
8	H	4-MeO	Br	50, 4h	95	1.44
9	H	2-MeO	Br	50, 4h	91	1.38

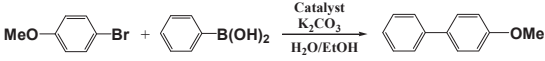
General procedure: 1.0 mmol of aryl halide, 1.05 mmol of arylboronic acid, 3.0 mmol of K₂CO₃, in H₂O / EtOH (4:3, V/V) under ambient atmosphere. TON = mol product / mol Pd. IR, ¹H and ¹³C NMR Spectra of the products in supplementary materials

In order to further investigate the catalytic activity of the (Pd²⁺/1)_n films, a series of parallel experiments were performed in the similar conditions. It was found that PdCl₂ rapidly formed Pd-black in the reaction, exhibiting low activity (Table 2, entry 2). Similarly, **1** was low active as a catalyst in the absence of a palladium source (Table 2, entry 1). A reaction of PdCl₂ and **1** produced gray precipitates, which acted as catalysts for the Suzuki reaction in the first cycle, displaying high catalytic activity (Table 2, entry 3). After reaction, the precipitates were collected, and reused in a second reaction sequence, very low activity was found (Table 2, entry 4). However, (PdCl₂/bpy)₁₀ film showed low catalytic

activity in the first cycle, and lower activity in the second cycle (Table 2, entry 5 and 6).

In contrast, the PEI-(Pd²⁺/I)₁₀ film could be successfully applied in multiple times successive coupling reactions. The procedure that utilized the PEI-(Pd²⁺/I)₁₀ film as a Pd-catalyst reservoir was as follows: The quartz slide coated with the PEI-(Pd²⁺/I)₁₀ film was immersed into a solution of 4-methoxy-aryl bromide, arylboronic acid, K₂CO₃ in EtOH and H₂O (step 1). After the mixture was stirred for 20 min at 50 °C, the quartz slide was removed from the mixture. The mixture was allowed to react for a further 10 h at 50 °C. The Pd-I complex released from the film is highly active as a catalyst under mild reaction condition, giving a high yield of the coupling product (Step 2). In the second catalytic cycle, the same coated quartz slide was then immersed into the next reaction mixture (Step 3). After the mixture was stirred for 20 min, the quartz slide was again removed from the reaction mixture and the second aliquot of released Pd-I complex used to catalyze a second Suzuki reaction (Step 4). Here in each immersion step, a certain amount of Pd-I complex in the film was desorbed into the reaction mixture and showed high catalytic activity for Suzuki reactions with high yields (Table 2, entry 7-10). After four cycles, the product yield came down rapidly, indicating that the catalytic active species into the solution were gradually depleted in the reactions (Table S4).

Table 2 Suzuki cross-coupling of 4-methoxyaryl bromide with phenylboronic acid using **1**, PdCl₂, PdCl₂/I precipitate, PEI-(PdCl₂/I)₁₀ film and (PdCl₂/bpy)₁₀ film as catalyst (bpy = 4,4'-bipyridine).

			
Entry	Run	Catalysts	Yield
1	1	1 ^a	Trace
2	1 st	PdCl ₂ ^b	16 %
3	1 st	PdCl ₂ /I precipitate ^b	97 %
4	2 nd	PdCl ₂ /I precipitate	Trace
5	1 st	(PdCl ₂ /bpy) ₁₀ film	40 %
6	2 nd	(PdCl ₂ /bpy) _{10-x} film	<30 %
7	1 st	(PdCl ₂ /I) ₁₀ film	95 %
8	2 nd	(PdCl ₂ /I) _{10-x} film	96 %
9	3 rd	(PdCl ₂ /I) _{10-x} film	94 %
10	4 th	(PdCl ₂ /I) _{10-x} film	92 %

^a General procedure: 1.0 mmol of PhBr, 1.05 mmol of PhB(OH)₂, 3.0 mmol of K₂CO₃, in H₂O/EtOH (4:3) at 50 °C under ambient atmosphere for 10 h. ^b Catalyst 3.0 mol%.

Concretely, after each reaction step, the resultant mixture was extracted three times with ethyl acetate (10 mL). Then the water phase was recycled as the reaction medium for a subsequent reaction. Additional aliquots of aryl halide and arylboronic acid were added into the recovered water phase, with refreshing the catalyst from the film. The mixture was allowed to react for 10 h at 50 °C, and the coupling product was obtained in good yield from these secondary reaction sequences. Recycling of the solvent in the organic synthesis has important significance for environmental protection.

In our work above, PEI-(PdCl₂/I)₁₀ film with extremely low Pd-loading was used as a catalyst reservoir being able to release progressively amounts of the catalytic active Pd species into the reaction solution and gave high catalytic efficiency in air with no inert gas protection. During the reaction processes, the amount of Pd-I complexes released

from the film could be controlled by the releasing time. In addition, the catalytic slides can be easily removed from the reaction system at any time, and reduce the waste of the catalysts. The palladium components as the catalysts were embed on the quartz slide surfaces, gradually released palladium particulates at the molecular level in the reaction and plausibly performed homogeneous reaction, so it showed considerably high catalytic activity.¹³ Additionally, the concave in the surface of the film could provide appropriate interspace effect to promote the C-C bond formation.^{14,15} Otherwise, the catalytic reactions were performed in the other solvents, and the results were listed in Table S5 (ESI).

In conclusion, PEI-(Pd²⁺/I)_n multilayers-loaded slides were used as catalyst reservoir to catalyze the Suzuki reaction in H₂O / EtOH solution, with catalyst loading as low as 6.6 × 10⁻⁶ mol% and high catalytic efficiency under the mild condition. The PEI-(Pd²⁺/I)_n film as a high active catalyst is expected to be greatly useful in organic synthesis for potentially Pd-catalyzed cross-coupling reactions.

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Notes and references

- † Crystal data for **1**: C₅₀H₃₈N₂P₂Pt, Monoclinic, space group P2(1)/c, *a* = 12.0599(12), *b* = 22.474(2), *c* = 7.8012(8) Å, β = 101.5980(10), *T* = 293 K, *Z* = 8, *V* = 2071.2(4) Å³, *D*_c = 1.481 g / cm³, λ = 0.71073 Å, 17791 reflections collected, 4744 unique which were used in calculations. *R*₁ = 0.0276 and *wR*₂ = 0.0717 for *I* > 2σ (*I*). CCDC 900608. Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Center.
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