Structure, Coordinative Self-Assembly of Films Based on Palladium Compound of Pyridyl-Acetylene Platinum and Application in Suzuki and Heck Coupling Reaction

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The platinum complex [Pt₂(C≡CPy)₂(dppm)₂] (Py = 4-pyridyl, dppm = bis(diphenylphosphino)methane) **1** has been prepared and characterized. Single crystal X-ray diffraction analysis reveals that **1** exhibits an approximately linear molecular geometry of Pt₂(C≡CPy)₂ fragment, in which the Pt-Pt bond may be considered as having been inserted within the delocalized π -electron system of 1,4-bis(4'-pyridyl)buta-1,3-diyne. The ability of the two terminal pyridyl nitrogen atoms of **1** to coordinate to other metal centers has enabled the use of **1** a linking ligand in the layer-by-layer (LbL) growth of heterometallic films. The self-assembly behavior of **1** with Pd(II), supported by chloride counter ions, on poly(ethylenimine) (PEI) functionalized solid surfaces has been investigated. The resulting multilayer films of general composition and form (PdCl₂/**1**)_n have been characterized by UV-vis absorption spectroscopy, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). On the basis of UV-vis spectroscopic data, (PdCl₂/**1**)_n multilayer films could be grown in a regular fashion, with film thickness increasing linearly with increasing deposition of metal-ligand bilayers. Consistent with this metal ion depend LbL growth, AFM images of the multilayer films exhibit island-shaped nanostructures with the mean diameter of about 25 nm. The catalytic properties of (PdCl₂/**1**)_n multilayers were investigated, and (PdCl₂/**1**)_n multilayers-loaded slides were used as catalyst reservoir capable of liberating catalytic amounts of a high active Pd species suitable to promote the C-C coupling formation, in which catalyst loading is as low as 2.76 × 10⁻⁶ mol% and gave high yields. The LbL catalyst and technology in this presentation show distinct hallmarks including extraordinarily low loading and high catalytic active characteristics.

1. Introduction

The identification of 'self-assembly' methods for the fabrication of discrete molecular species, extended frameworks and surface confined monolayers from smaller molecular building blocks through careful choice of mutually compatible intercomponent recognition sites has seen the development of an entire field of supramolecular chemistry.¹ Similar concepts involving the manipulation of strong molecule-surface interactions have provided methods for the facile fabrication of low defect molecular films on a wide range of surfaces through appropriate choice of surface contacting group.² Transition-metal coordination chemistry provides an exciting range of opportunities for the preparation of self-assembled films and multilayers on surfaces,³ with exquisite control over the film thickness, composition and morphology through choice of both metal and nature of the supporting and bridging ligands. The use of linear, ditopic ligands permits the construction of multi-layer

films in a stepwise fashion, and such layer-by-layer (LbL) technology has become a popular technique for thin film preparation because of its simplicity, robustness, and versatility.⁴ These coordination-based mono- and multi-layers self-assembled films are prepared by alternate adsorption of organic ligand and metal ion layers onto solid substrates, and as such the robustness and morphology of the films rests on both the ligand-substrate and the metal ion-ligand interactions.⁵ A wide variety of self-assembled multilayers containing metal ions have now been prepared by such 'synthesis on the surface' methods,⁶ exploiting ligands such as bis(phosphonate)s,^{6a} pyrazines with Ru²⁺,^{6b} dithiols with Cu²⁺,^{6c} diamines with Ru²⁺,^{6d} and diisocyanides with Co²⁺.^{6e} Recently, palladium-ligand multilayers were successfully prepared by alternate adsorption of an organic ligand, such as bridging 4,4'-bipyridine and palladium ion layers onto solid slides.⁷

Within the field of supramolecular chemistry, the use of *metalloligands* as supports for the assembly of larger structures is perhaps most widely represented by the use of polycyanometallates in the fabrication of Prussian Blue analogues,⁸ although the fabrication of larger molecular structures by covalent assembly of metal complex building blocks is also known.⁹ Metal complexes based on the Pt-acetylide moiety are potential candidates for use in the assembly of functionalized supramolecular compounds, due to their robust chemical structures and interesting optoelectronic and catalytic properties.¹⁰⁻¹² Platinum(II) alkynyl complexes suitable for use as

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metalloligands in self-assembly processes are known, including [Pt₂(μ-dppm)₂(C≡CPy)₄] (Py = 4-pyridyl, dppm = bis(diphenylphosphino)methane) and [Pt(bipy)(C≡CPy)₂] (bipy = 2,2'-bipyridyl).¹¹ However, self-assembly of platinum(II) alkynyl complexes on solid surfaces has been rarely reported. The pyridyl-acetylene platinum complex [Pt₂(C≡CPy)₂(dppm)₂] **1** (Scheme 1) features a robust bimetallic Pt₂ core, linear topology and pyridyl nitrogen atoms suitable for further coordination to other metal centers.

In this report we describe the use of the coordinating properties of the pyridyl moieties in the inorganic rigid-rod **1** to promote layer-by-layer (LbL) growth of polymetallic films containing alternating arrays of palladium metal ions and **1**. These self-assembled LbL films have been characterized by UV-vis spectroscopy and atomic force microscopy (AFM). The application of (PdCl₂/1)_n multilayer-loaded slides as catalyst reservoirs has been explored using the Suzuki and Heck reaction as a demonstration platform.

Scheme 1 Sketch drawing of compound **1**.

2. Experimental section

2.1. Materials and methods

Poly(ethylenimine) (PEI, 50 wt% aqueous solution) was purchased from Aldrich Chemical Co. All aqueous solutions were prepared with doubly-distilled water. Synthetic reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. All reaction vessels were flame-dried before use. Triethylamine was purified by distillation over CaSO₄. Tetrahydrofuran was purified and dried using Innovative Technology SPS-400 solvent purification system. Methanol was distilled over KOH under N₂ prior to use. The compounds [Pt₂(dppm)₂Cl₂] and [Pd(PPh₃)₄] were prepared according to literature procedures.^{13,14} Other reagents were purchased and used as received. NMR spectra were recorded in deuterated solvent solutions on Bruker DRX-400 and Varian Inova 400 spectrometers and referenced against solvent resonances (¹H, ¹³C). Matrix assisted-Laser Desorption / Ionisation (MALDI) mass spectra was obtained using an Autoflex II TOF/TOF mass spectrometer (Bruker Daltonik GmbH) using a *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) matrix. Atmospheric pressure solids analysis probe (ASAP) mass spectra were obtained using a XevoQToF mass spectrometer (Waters Ltd, UK). IR spectra were recorded on a Thermo 6700 spectrometer from CH₂Cl₂ solutions using solution cells fitted with CaF₂ windows or as Nujol mulls suspended between NaCl plates. UV-vis absorption spectra were recorded on a quartz slide using a Lambda35 spectrophotometer (Perkin Elmer, USA).

2.2. Preparation of 4-ethynylpyridine hydrochloride

To a 50 mL Schlenk charged with degassed NEt₃ (15 mL) and THF (15 mL), 4-bromopyridine hydrochloride (0.50 g, 2.57 mmol), Pd(PPh₃)₄ (0.15 g, 0.13 mmol), CuI (0.02 g, 0.11 mmol)

and trimethylsilylacetylene (0.37 mL, 2.58 mmol) were added and the mixture was stirred at reflux overnight in the dark. The reaction mixture was taken to dryness and the black residue was purified through a silica gel column using hexane: EtOAc (9:1) as the eluent. Removal of solvent from the main fraction yielded 4-trimethylsilylethynyl pyridine as an orange oil (0.40 g, 2.80 mmol, 89 %) that tends to crystallize on standing, but develops deep coloration after a few hours, and was therefore used immediately in the next reaction sequence [¹H NMR (400 MHz, CDCl₃) δ 7.56 (dd, *J* = 4 Hz, *J* = 2 Hz, 2H, *a*), 7.30 (dd, *J* = 4 Hz, *J* = 2 Hz, 2H, *b*), 0.26 (s, 9H, *f*)] (See Scheme 2 for atom labelling scheme). The oil was immediately dissolved in CHCl₃ (50 mL) under inert atmosphere yielding an orange solution that turned black upon drop wise addition of tetra-*n*-butylammonium fluoride (TBAF) (1M in THF) (2.9 mL, 2.9 mmol). The mixture was stirred at room temperature in the dark for further 15 minutes and poured into water. The organic red phase was washed with water (2×50 mL), brine (1×50 mL) and dried over MgSO₄.

The organic phase containing 4-ethynyl pyridine was transferred into a three-necked flask, fitted with a gas inlet and bubbler, and sealed with a Quick-Fit stopper. The gas inlet was connected by PVC tubing through a second gas inlet to a second, two-neck flask containing NaCl and fitted with a dropping funnel containing conc. H₂SO₄. Dropwise addition of the H₂SO₄ to the solid NaCl generated HCl(g), which passed through the tube to the flask containing the crude HC≡CC₅H₄N, and vented through the bubbler. The brown precipitate formed was removed by filtration, and the filtrate purged with N₂ to remove excess HCl(g). An off-white solid was formed upon concentration of the solvent under reduced pressure (~5 mL). The off-white coloured solids were collected by filtration, washed with Et₂O and dried in air for a short time to give the desired hydrochloride salt of 4-ethynyl pyridine before storage under inert atmosphere, in the dark at -24 °C (0.253 g, 0.056 mmol, 65%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.25 (s *br.*, 1H, *g*), 8.86 (d, *J* = 6 Hz, 2H, *h*), 7.97 (d, *J* = 6, 2H, *i*), 5.20 (s, 1H, *m*). ¹³C NMR (101 MHz, CDCl₃) δ 144.1, 128.5 (*h-i*), 136.5 (*j*) 91.4, 79.9 (*k-l*). IR (CH₂Cl₂): ν(C_{sp}-H) 3291.0 cm⁻¹, (C≡C) 2121.7 cm⁻¹. MS (ASAP)⁺ (*m/z*) (140.0, 10% [M+H]⁺), (279.1, 100% [2M+H]⁺) (Scheme 3 for the atom label).

2.3. Preparation of Pt₂(C≡CPy)₂(dppm)₂ (**1**)

To a Schlenk flask charged with potassium *tert*-butoxide (KO^tBu) (0.07 g, 0.62 mmol) dissolved in 8 mL of MeOH, 4-ethynylpyridine hydrochloride (0.025 g, 0.23 mmol) was added. Upon dissolution of the ligand, Pt₂Cl₂(dppm)₂ (0.10 g, 0.08 mmol) was added and the orange suspension was stirred in the absence of light at room temperature for 3 hours. The orange precipitate was filtered and washed thoroughly with MeOH. The solids were dissolved in CH₂Cl₂ and filtered through basic alumina (Brockmann I). The pale yellow precipitate formed upon addition of hexane was collected by filtration, washed with Et₂O and dried in air (0.099 g, 0.069 mmol, 85 %). The sample was somewhat sensitive in solution, decomposing overnight in CH₂Cl₂, under inert atmosphere in the dark. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J*_{H-H} = 6 Hz, 4H, *c*), 7.58-7.47 (m, 16H, *CH_{ar}*), 7.34-7.28 (m, 8H, *CH_{ar}*), 7.18-7.10 (m, 16H, *CH_{ar}*), 4.97 (m, *J* = 4 Hz, ²*J*_{P-H} = 8 Hz, ³*J*_{P-H} = 55 Hz, 4H, *a*). ³¹P{¹H} NMR (162 MHz, CDCl₃) δ 2.1 (s, ¹*J*_{P-P} = 2829 Hz, *dppm*). IR (Nujol): ν(C≡C) 2086 cm⁻¹.

MS (MALDI-TOF)⁺ (*m/z*) (1363.2, 100% [M+H]⁺).

Table 1 Crystal data and structure refinement for **1**

Identification code	1
Empirical formula	C ₆₄ H ₅₂ N ₂ P ₄ Pt ₂
Formula weight	1363.14
Temperature/K	120
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	16.7418(9)
<i>b</i> /Å	20.0777(11)
<i>c</i> /Å	17.0974(10)
β /°	114.4550(10)
Volume/Å ³	5231.5(5)
<i>Z</i>	4
ρ_{calc} /mg/mm ³	1.731
μ /mm ⁻¹	5.509
<i>F</i> (000)	2664.0
Reflections collected	56545
Independent reflections	11969 [<i>R</i> (int) = 0.0938]
Data/restraints/parameters	11969/2/631
Goodness-of-fit on <i>F</i> ²	1.005
Final <i>R</i> indexes [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0388, <i>wR</i> ₂ = 0.0719
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0749, <i>wR</i> ₂ = 0.0844

2.4. X-ray crystallography

Single crystal X-ray data were collected on a Bruker SMART 5 6000 diffractometer equipped with a Cryostream (Oxford Cryosystems) nitrogen cooling device at 120K using graphite monochromated MoK α radiation (λ = 0.71073Å). The structure was solved by direct method and refined by full-matrix least squares on *F*² for all data using SHELXTL and OLEX2 10 software.^{15,16} All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in the calculated positions and refined in "riding" mode. The crystallographic data of **1** are listed in Table 1 and the selected bond lengths and angles in Table S1. Crystallographic 15 data (excluding structure factors) for **1** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication CCDC-880523. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, 20 Cambridge CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk].

2.5. Modification of substrate surface

The quartz slides were cleaned with fresh piranha solution (7:3, V/V H₂SO₄-H₂O₂) (Caution! Piranha solution is extremely 25 corrosive) at 80 °C for 40 min, and thoroughly rinsed with distilled water. Further purification was carried out by immersion

in an H₂O/H₂O₂/NH₃OH (5:1:1) (V/V/V) bath for 30 min at 70 °C. The clean quartz slides were then immersed in PEI solution for 20 min, before being washed with deionized water (Milli-Q, 18.2 MΩ cm) and dried under a nitrogen stream.

2.6. Fabrication of (PdCl₂/1)_n films

The slides pre-coated with PEI as a metal-ion adhesion layer were placed into aqueous solution containing PdCl₂ for 60 min. After being washed with deionized water and dried under a nitrogen stream, the resulting PEI-metal ion slides were immersed in a 35 solution of **1** (0.5 mM) in aqueous ethanol solution for 60 min. By repeating the sequential immersion of the slides in solutions of metal salt and **1**, PEI-(PdCl₂/1)_n multilayers were prepared. Between each immersion step, the substrates were washed with water and dried with N₂ stream at room temperature.

2.7. General procedure for the Suzuki coupling reactions

A general procedure for the coupling reactions of aryl halides with arylboronic acid is as follows: Aryl halide (1.0 mmol), arylboronic acid (1.05 mmol), K₂CO₃ (3.0 mmol), the quartz slide with (PdCl₂/1)₁₀ film (25 mm × 12 mm × 1 mm), EtOH (3 mL) 45 and H₂O (4 mL) were introduced to an open flask under ambient atmosphere. The quartz slide coated with the residual multilayer was removed from the reaction mixture after 20 min and the mixture was stirred at 50 °C for 20 h. In the second catalytic cycle, the same quartz slide was immersed into the second 50 reaction mixture of aryl halides and arylboronic acid. The quartz slide was again removed from the reaction mixture after 20 min and the mixture was stirred at 50 °C for 20 h. In each reaction cycle, the resultant mixture was extracted three times with ethyl acetate (10 mL), the organic phases combined and washed with 55 brine, dried over Na₂SO₄, filtered, and the volatiles removed under reduced pressure. The biaryl product was the only volatile species detectable by gas chromatography-mass spectrometry (GC-MS) analysis of the extract. The extracts were purified by column chromatography on silica gel (ethyl acetate / hexane 1:8) 60 to afford the desired products. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in CDCl₃ solutions.

2.8. Analysis of Pd content in (PdCl₂/1)₁₀ multilayers

The quartz slide coated with (PdCl₂/1)₁₀ was immersed into a NaOH aqueous solution (0.5 mM, 7 mL). UV-vis spectra were 65 used to monitor the absorbance change of the coated quartz slide. When the coated quartz slide exhibited no absorbance, the solution (7 mL) was used for analysis of Pd content.

Scheme 2 Preparation routes of the 4-ethynylpyridine.

2.9. Instrumentation

UV-vis absorption spectra were recorded on a quartz slide with a Lambda35 spectrophotometer (Perkin-Elmer, USA). High-resolution X-ray photoelectron spectra (XPS) were collected at a takeoff angle of 45° using PHI Quantum 2000 scanning ESCA microprobe (Physical Electronics, USA) with an Al α X-ray line (1486.6 eV). All AFM images were taken on a single-crystal silicon slide using a Veeco Multimode NS3A-02NanoscopeIII atomic force microscope with silicon tips. Height images of the films were recorded using tapping-mode AFM. Gas chromatograph was performed on VARIAN 430 Gas Chromatograph. Analysis of Pd content was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using Ultima.

3. Results and discussion

3.1. Synthesis and structure of 1

The key reagent 4-ethynylpyridine was prepared from a Sonogashira cross-coupling reaction of 4-bromopyridinium hydrochloride with trimethylsilylacetylene, and isolated as the hydrochloride salt after desilylation (Scheme 2).

Compound **1** was prepared from the reaction of Pt₂Cl₂(dppm)₂ with 4-ethynylpyridinium hydrochloride in methanol solutions containing an excess of KO^tBu in a manner similar to that reported elsewhere for the preparation of related complexes (Scheme 3).¹⁷ Although stable as a solid in air, solutions of **1** in chlorinated solvents were more prone to decomposition. The spectroscopic data for **1** were in accord with the proposed molecular structure, with a $\nu(\text{C}\equiv\text{C})$ band at 2086 cm⁻¹ in the IR spectrum clearly indicating incorporation of the alkynyl ligands. In the ³¹P NMR spectrum the singlet arising from the dppm ligands was flanked by a collection of platinum satellites to varying combination of ^{194/195/196}Pt, although the individual resonances arising from the various combinations of were not fully resolved (See ESI).

Single crystals of **1** suitable for single crystal X-ray analysis were grown from CH₂Cl₂ / hexane. Each platinum center (Fig. 1) is coordinated by two P atoms from the dppm ligands and a 4-ethynylpyridine (-C≡CPy) ligand. The fourth coordination site is occupied by a Pt-Pt bond, forming a slightly distorted square planar geometry at each metal center with Pt-P distances ranging from 2.2607(17) to 2.2741(16) Å, Pt-C = 2.012(6) and 2.014(7) Å, Pt(1)-Pt(2) = 2.7080(4) Å (Table S1 in ESI). The bond lengths in compound **1** are within normal ranges (Pt-C: 1.995 – 2.012 Å; Pt-P: 2.200 – 2.300 Å),^{17b,c} and compare well with platinum alkynyl analogues (Pt₂(dppm)₂(C≡CCpFeCp): Pt-Pt = 2.7023(2), Pt-C = 2.055(4), 2.021(4), Pt-P = 2.2510(9) Å.^{17a} The short Pt-Pt separation is imposed by the bridging dppm ligands, but is consistent with the presence of a Pt-Pt σ bond.¹⁸ Detailed electronic structure calculations on the general framework [Pt₂(C≡CPh)₂(dppm)₂] indicate the HOMO and HOMO-1 contain the d_{xy} orbital which although antibonding with respect to each other are of the correct symmetry to interact further with the alkynyl π -system offered by the alkynyl ligands.¹⁹ This gives rise to a rather delocalized orbital with d π^* character along the C≡C-Pt-Pt-C≡C backbone. Consequently, the Py-C≡C-Pt-Pt-C≡C

-Py fragments are close to linear with the bond angles C1-Pt1-Pt2 = 174.40(17)°, C8-Pt2-Pt1 = 178.47(18)° (Table S1 in ESI). This linear arrangement, coupled with the excellent coordinating properties of the pyridyl N atoms towards many transition metal ions makes **1** a useful building units for the assembly of larger one-dimensional chains or multi-layer films.

Fig. 1 The molecular structure for Pt₂(C≡CPy)₂(dppm)₂ (**1**).

Fig. 2 UV-vis spectrum of **1** in the EtOH solution.

3.2. Spectroscopic evaluation of LbL growth

The UV-vis absorption spectrum of **1** in EtOH solution is shown in Fig. 2. Poorly resolved bands near 266 nm, 322 nm and 400 nm extending from the UV region through to approximately 480 nm correspond to overlapping π - π^* and MLCT transitions. The absorption features were used as reference points to monitor the growth of films containing **1** on quartz substrates.

The nature of the connection between the substrate and molecular components is important for the construction of robust multilayer molecular films. A wide variety of functional groups have been demonstrated to be suitable for the construction of monolayer films on different substrates by self-assembly,²⁰⁻²² although in general the formation of robust self-assembled films requires the choice of a surface binding group appropriate to the particular substrate surface being employed. In our present study, we used PEI, which can form smooth and uniform layers on many different substrate surfaces,²² to pre-coat the substrate

slides in order to obtain a functional surface. The PEI-coated surface offers reactive primary, secondary, and tertiary amine functional groups that can form complexes with a wide variety of transition metal ions. This leads to a methodology for forming metal-ion containing films in a simple, but highly efficient, process. In the present work, PEI-(PdCl₂/1)_n multilayer films were prepared by alternately immersing quartz slide pre-coated with a PEI layer in aqueous solutions of the desired metal ions or 1. The final chemical and physical properties of the self-assembled (PdCl₂/1)_n films depend on the nature of both the structure of the PEI sublayer, the PEI-substrate interactions, and the coordinative metal–1 interactions.

Fig. 3 Typical height images of the films on the single-crystal silicon substrate (scan area is $1.0 \times 1.0 \mu\text{m}^2$). a: (Pd/1)₅ ($R_{\text{rms}} = 1.01 \text{ nm}$), b: (Pd/1)₁₀ ($R_{\text{rms}} = 1.88 \text{ nm}$).

3.3. AFM characterization

The morphology of LbL self-assembled films were analyzed by AFM images at a scan area of $1.0 \times 1.0 \mu\text{m}^2$ with tapping mode (Fig. 3), which provides valuable information about the surface topology as a function of both number of layers in the multi-layer construction and the metal ion employed. Before metal ion deposition, the PEI film is smooth and uniform and the root-mean-square (RMS) is 0.509 nm. With increasing the number of deposited bilayers, the surface roughness also increases and the surface exhibits more obvious particulate characteristics. AFM images reveal a series of bright islands, corresponding to local concentration of the metal ions. For example, the PEI-(Pd/1)₅ film is relatively uniform and smooth with the root-mean-square (RMS) roughness 1.01 nm (Fig. 3a), whereas the island-shaped nanostructures are more pronounced on the surface of PEI-(Pd/1)₁₀ film with RMS 1.88 nm (Fig. 3b). The mean diameter of island-shaped nanostructures is about 25 nm.

As seen in Fig. 4, for PEI-(PdCl₂/1)_n multilayer films, UV-vis spectrum is used to characterize the growth process of the films and resulting measurements show a good linear correlation with $R^2 = 0.9918$ between the optical absorption at $\lambda_{\text{max}} = 343 \text{ nm}$ and the number of PdCl₂/1 layers. This indicates the formation of a structurally regular multilayer with an equal density of 1 and palladium ions deposited in each bilayer, consistent with the square-planar geometry associated with metal palladium ions, and leading to well-ordered structure in the direction of film growth.

Fig. 4 UV-vis spectra of the (Pd/1)_n ($n = 1 \sim 14$) films. Inset: increase in the absorbance at 343 nm as a function of the number of layers of (Pd/1)_n.

Fig. 5 XPS of a (PdCl₂/1)₆ film deposited on the single-crystal silicon substrate. (a) survey, (b) Pd_{3d}.

XPS measures were performed to identify relative elemental composition of multilayer films deposited on the single-crystal silicon substrate precoated with PEI. The spectra show all the expected elements in the multilayers. As shown in Fig. 5a, the survey spectrum of the film showed the presence of C_{1s} (284.8 eV), O_{1s} (531.8 eV), N_{1s} (399.9 eV), P_{2p} (131.9 eV), Pt_{4f} (73.8 eV), and Pd_{3d} (337.7 eV). XPS provides information about the Pd oxidation state in the (PdCl₂/1)_n multilayer with photoelectrons at energies of 337.7 and 342.9 eV corresponding to Pd(II) being detected (Fig. 5b). These XPS results confirm the presence of 1 and Pd(II) in the multilayer film.

3.4. Catalytic application of (PdCl₂/1)₁₀ film-loaded quartz slide for the Suzuki and Heck reactions

Palladium is widely used as a catalyst to promote a variety of C-element bond forming reactions.²³ For example, the Pd-catalyzed Suzuki coupling reaction of aryl halides with aryl boronic acids is one of the most powerful methods for C-C bond formation.²³ This reaction is performed under mild conditions in aqueous solutions. Pd/phosphine complexes have received increasing interest in Suzuki reaction.²⁴ Numerous heterogeneous and/or recoverable Pd catalysts have been reported.²⁵ However, many of these methods still require a relatively high catalyst concentration (Pd-loading, 3 ~ 10 mol%). In this report, we utilized (PdCl₂/1)₁₀ film as a catalyst reservoir able to liberate progressively catalytic amounts of an active Pd species into the reaction solution (Pd-loading of 2.76 × 10⁻⁶ mol%).

Table 2 Suzuki cross-coupling of PhBr with PhB(OH)₂ using 1, PdCl₂, Pd(PPh₃)₄, Pd(OAc)₂, PdCl₂/bpy precipitate and PdCl₂/1 precipitate as catalysts^a (bpy = 4,4'-bipyridine)

$\text{C}_6\text{H}_5\text{Br} + \text{C}_6\text{H}_5\text{B(OH)}_2 \xrightarrow[\text{H}_2\text{O/EtOH}]{\text{Catalyst, K}_2\text{CO}_3} \text{C}_6\text{H}_5\text{C}_6\text{H}_5$				
Entry	Run	Catalysts	Condition	Yield ^b
1	1 st	1	in air	0
2	1 st	PdCl ₂	in air	<5
3	1 st	Pd(PPh ₃) ₄	in air	28
4	1 st	Pd(OAc) ₂	in air	41
5	1 st	PdCl ₂ /bpy precipitate	in air	39
6	1 st	PdCl ₂ /1 precipitate	in air	99
7	2 nd	PdCl ₂ /1 precipitate	in air	trace

^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 20 h. ^b Isolated yield (%). Catalyst 3.0 mol%.

By way of a series of control experiments, it was found that PdCl₂ formed palladium black rapidly in air atmosphere for these reaction systems, with very low catalytic activity (Table 2, entry 2). When Pd(PPh₃)₄ or Pd(OAc)₂ in stead of PdCl₂ acted as catalysts in the system above, the reaction gave low yields (Table 2, entries 3 and 4). Similarly, 1 was inactive as a catalyst in the absence of a palladium source (Table 2, entry 1). When the precipitate of PdCl₂/bpy as a catalyst, the reaction also provided a low yield (Table 2, entry 5). Reaction of PdCl₂ with 1 (1:1 /mol) in EtOH/H₂O solution formed a precipitate, which was collected but not fully characterized. The PdCl₂/1 precipitates as catalysts gave a considerable high yield (Table 2, entry 6), in which the π-d-π species in 1 could remodel the valence electron structure of Pd and enhanced the catalytic activity of PdCl₂/1 complexes upon synergetic interaction of the (PyC≡C)-Pt-Pt-(C≡CPy) moiety with Pd(II) component. Although this Pd-1 precipitate exhibited high catalytic activity for the Suzuki reaction in the first cycle, the material could not be effectively recycled. After reaction, the precipitate was collected, and re-used in a second reaction sequence, but was found to exhibit very low activity (Table 2, entry 7). In contrast, the (PdCl₂/1)₁₀ film can be successfully applied in coupling reactions and re-used for up to five successive coupling reactions under similar conditions (Table 3, entries 1-5). The observation of high yields of cross-coupled products (Table 3, entries 6-8) in reactions with substituted aryl halides and boronic acids (Table S2 in ESI) suggests little contribution to the over-all reaction yields from homo-coupling side reactions.

To use the multilayer films as a Pd-catalyst reservoir was performed in air atmosphere. The quartz slide coated with (PdCl₂/1)₁₀ film was immersed into a solution of aryl halide,

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 reaction mixture. The mixture was allowed to react for a further 20 h at 50 °C. The Pd-1 complex released from the slide is highly active as a catalyst for the Suzuki cross-coupling reactions under mild reaction conditions, giving a high yield (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 slide was again removed from the reaction mixture and the second aliquot of released Pd-1 complex used to catalyze a second Suzuki reaction (Step 4). Therefore in each immersion step, a certain amount of Pd-1 complexes in the film is desorbed into the mixture and shows high activity for Suzuki reaction with the biphenyl in good yield (Table 3). The process could be repeated up to five successive desorption steps for each (PdCl₂/1)₁₀ film.

Table 3 Suzuki cross-coupling of aryl bromide with phenylboronic acid using Pd-1 complexes as catalysts released from (PdCl₂/1)₁₀ films^a

$\text{R}_1\text{-C}_6\text{H}_4\text{-Br} + \text{R}_2\text{-C}_6\text{H}_4\text{-B(OH)}_2 \xrightarrow[\text{H}_2\text{O/EtOH}]{\text{Pd catalyst, K}_2\text{CO}_3} \text{R}_1\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-R}_2$						
Entry	Run	R ₁	R ₂	Catalyst	Yield ^b	TON
1	1 st	H	H	(Pd/1) ₁₀	99	3.58×10 ⁴
2	2 nd	H	H	(Pd/1) _{10-x}	99	3.58×10 ⁴
3	3 rd	H	H	(Pd/1) _{10-x}	95	3.44×10 ⁴
4	4 th	H	H	(Pd/1) _{10-x}	92	3.33×10 ⁴
5	5 th	H	H	(Pd/1) _{10-x}	95	3.44×10 ⁴
6	1 st	CF ₃	H	(Pd/1) ₁₀	98	3.55×10 ⁴
7	1 st	OMe	H	(Pd/1) ₁₀	95	3.44×10 ⁴
8	1 st	H	OMe	(Pd/1) ₁₀	97	3.51×10 ⁴

^a General procedure: 1.0 mmol of aryl bromide, 1.05 mmol of PhB(OH)₂, 3.0 mmol of K₂CO₃, in H₂O/EtOH (4:3) at 50 °C under ambient atmosphere for 20 h. ^b Determined by GC (%). TON = mol product / mol Pd. Pd-catalyst 2.76 × 10⁻⁶ mol% for (Pd/1)₁₀ film.

Interestingly, 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 both aryl halide (1.0 mmol) and arylboronic acid (1.05 mmol) were added into the recovered water phase, without refreshing the catalyst by exposure to a slide. The mixture was allowed to react for 20 h at 50 °C. Although Pd-content in the water phase was not detected by ICP after each reaction, because it was too low to measure, it was found that the cross-coupled product was also obtained in good yield from these secondary reaction sequences. According to the above-mentioned results, the amount of 2.94 μg (0.42 ppm × 7 mL) Pd in (PdCl₂/1)₁₀ film is enough to be recycled for 10 times which is from 5 uses of the slide, and one recycle in each case. Recycling of the solvent has important significance for environmental protection. Catalyst loading is low, thus reducing the amount of waste. Such low catalyst loading is important for synthesizing pharmaceutically active ingredients, and these simple slide-based catalyst systems have many appealing characteristics.²⁶

We were not able to perform on-line detection of the Pd concentration during the catalytic reaction process. Therefore, we found an alternative method of approximating the amount of Pd released into the reaction solution. After (PdCl₂/1)₁₀ films are completely desorbed into the aqueous solution (7 mL), the amount of Pd was determined as 0.42 ppm (ICP) in the solution. Therefore, the catalyst loading of each cycle is estimated to be

approximately 0.08 ppm according to the total amount of 0.42 ppm Pd in (PdCl₂/1)₁₀ multilayers and the capacity for the slides to be reused effectively up to five times in the Suzuki reactions. We note however that the film inhomogeneity revealed by the AFM images prevents confident description of the desorption processes in terms of a smooth delamination of the films.

In order to determine whether the catalyst was functioning in a homogeneous solution phase, we carried out the following tests: The quartz slide coated with (PdCl₂/1)₁₀ multilayers was immersed a mixed solution of K₂CO₃, EtOH and H₂O for each interval of 20 minutes, respectively, to study the release behavior of Pd-1 complex. UV-vis spectra were used to monitor the change of films (Fig. S1). A obvious decrease of the absorbance at 343 nm was observed for the first 20 min due to the desorption of the multilayers, and the absorbance slowly decreases in the subsequent measurement. The UV-vis spectra above exhibited that the desorption was not be completely uniform, but close to be linear, which validated that (PdCl₂/1)₁₀ multilayer could release the Pd-1 species mostly in a layer-by-layer manner, along with the nanoclusters in each cycle step. On the other hand, a Pd(0) complex as the active species may not be involved in the reaction for the present case, because the nitrogen donor can not stabilize Pd(0) complexes well, which was also confirmed by XPS data of the (PdCl₂/1)_n multilayer. The catalytic mechanism may be based on a Pd(II)/Pd(IV) cycle in the reaction process.²⁷

Table 4. Heck reactions of aryl halides with olefins using Pd-1 complexes as catalysts released from (PdCl₂/1)₁₀ multilayer films^a

Entry	R ₁	X	R ₂	Yield(%) ^b	TON
1	4-CN	Br	Ph	98	3.55×10 ⁴
2	4-COMe	Br	Ph	90	3.26×10 ⁴
3	4-OMe	Br	Ph	80	2.90×10 ⁴
4	H	I	CO ₂ tBu	90	3.26×10 ⁴
5	H	Br	CO ₂ tBu	47	1.70×10 ⁴

^a General procedure: 1.0 mmol of aryl halide, 1.5 mmol of olefin and 3.0 mmol of Na₂CO₃ in 12 mL DMF at 140 °C for 24 h under ambient atmosphere. ^b Isolated yield. TON = mol product / mol Pd. IR, ¹H NMR spectra of the products listed in ESI.

To further investigate the catalytic activity and application scope of the slides coated with PEI-(PdCl₂/1)₁₀ films as catalysts, Heck reactions of aryl halide derivatives with terminal olefins were performed in a similar manner as described for the Suzuki reactions. The slides coated with PEI-(PdCl₂/1)₁₀ films were immersed into the reaction mixtures (1.0 mmol of aryl halide, 1.5 mmol of styrene) in DMF solution at 140 °C for 24 h in the presence of Na₂CO₃ as base in air, and then the expected products were separated by extraction and purification after finishing the reaction. The results showed that aryl bromides with electron-withdrawing groups (e.g. -CN and -COMe) provided high yields (Table 4, entries 1 and 2), and electron-donating groups (e.g. -OMe) gave favorable yield (Table 4, entry 3). The reaction of aryl bromide with *tert*-butyl acrylate provided slightly lower yield (Table 4, entry 5). When aryl bromide was replaced by aryl iodide, the reaction between aryl iodides and olefin (e.g. -CO₂tBu) showed high activity under the same reaction condition (Table 4, entry 4), because iodobenzene is more active than bromobenzene.²⁸ However, palladium(II)-bipyridine complexes reported by Kawano were not effective for the Heck reaction in

the similar reaction systems.²⁹ In our work above, PEI-(PdCl₂/1)₁₀ multilayer films served as catalyst reservoirs with low catalyst loading, leading to high yields and TON values up to 10⁴. The released material clearly displays high catalytic activity for the Heck reaction of aryl halides and styrenes.

To scrutinize the components released from the LbL films during these reaction cycles, and the micro-morphologies of fractures released from multilayer films, is of considerable interest, but extremely challenging given the very low species concentration. In the assembly process, the multilayer films were assembled along with the deposition nanoparticles on the surfaces to form island-shaped nanostructures. The catalytically active material released in the course of the reaction would contain both nanoclusters and the delaminated Pd-1 molecular layer based material. UV-vis absorption spectra give some evidence for the nature of the released material. Compound 1 exhibits a broad absorption band between 360 ~ 520 nm in the solution of EtOH/H₂O (3:1, V:V) (Fig. S2, in ESI). The PdCl₂/1 precipitates give rise to a broad absorption band between 360 ~ 550 nm when suspended in the solution of EtOH/H₂O (3:1) (Fig. S3). The material released from the films in the solution of EtOH/H₂O (3:1) give features between 360 ~ 525 nm attributed to overlapping π-π* and MLCT transitions (Fig. S4). UV-vis absorption spectra above indicate that the fractures released from the film are mainly composed of the Pd-1 complexes or its nanoparticles, in which the slight discrepancy of UV-vis absorption may result from the quantum effect of the nanoparticles. The reasoning above was also validated by the fluorescence emission spectra of the related samples in the solution of EtOH/H₂O (Fig. S5-7, in ESI). The fluorescence emission spectrum of the PdCl₂/1 precipitates resemble one of 1 very much, but the blue shift occurred for the fluorescence emission spectrum of the fractures released from the film due to the nanometer size effect of the nanoparticles.

Two terminal pyridyl nitrogen atoms of 1 are in the approximately linear geometry, which favors the directed assembly to coordinate to other metal centers in the layer-by-layer (LbL) growth of heterometallic films, and certainly also approves the directed array in the formation of the Pd-1 precipitates (Fig.S8, SEM in ESI). Oppositely, in the desorption course, larger amounts of a high active Pd-1 and/or its nanoparticles were discharged into the reaction solution. We hypothesize that the released Pd-1 components from the multilayers are the soluble molecular Pd species which act as the active constituents in a homogeneous process. Whilst we cannot completely exclude the formation of nanoparticulate material, we have no evidence in support of heterogeneous mechanism.

In this work, the PEI-(PdCl₂/1)_n multilayer-loaded slides were used as catalyst reservoir showing some distinct favorable features: (1) The reactions were conducted in air with no inert gas protection; (2) Catalyst uploaded with extraordinarily low amount (down to 2.76 × 10⁻⁶ mol%); (3) the amount of Pd-1 complexes released from the film could be controlled by the releasing time. Still, the catalytic slides can be easily removed from the reaction system at any time, and reduce the waste amount of the catalysts. Thus, to load Pd-1 complexes on slides would increase utilizing ratio of catalysts in chemical reactions. Additionally, the concave in the film could provide appropriate interspaces to promote

formation of C-C bond through interface or quantum effect from the palladium nano-particulates in the reaction system.

4. Conclusions

Compound **1** were successfully prepared and characterized by single crystal X-ray diffraction analysis. Compound **1** can be used in the self-assembly of multi-layer films through sequential reaction with PdCl₂. Multilayers (PdCl₂/**1**)₁₀ were deposited on solid slides in alternating arrays of palladium metals and **1**. The results of UV-vis spectroscopy show that (PdCl₂/**1**)₁₀ multilayers are constant and uniform. PEI-(PdCl₂/**1**)_n multilayers-loaded slides were used as catalyst reservoir to catalyze the Suzuki reaction with extraordinarily low catalyst loading estimated to be 2.76 x 10⁻⁶ mol%. These simple slides have capacity to serve as convenient reservoirs of active catalyst for Suzuki and potentially other Pd-catalyzed cross-coupling reactions which make them appealing within philosophies of synthesis chemistry.

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