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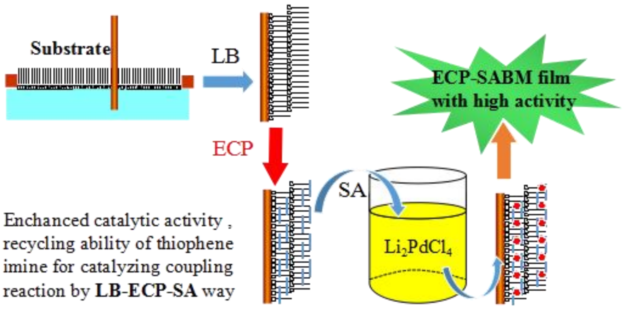

Enchanced catalytic activity , recycling ability of thiophene imine for catalyzing coupling reaction by **LB-ECP-SA** way

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ARTICLE TYPE

Electrochemical polymerized and assemblied cyclopalladated bi-thiophene imine for catalyzing coupling reaction: A modern strategy to enchancing catalytic activity

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Abstract:The catalytic activity and recycling of self-assembly electrochemical polymerized 1, 2-bis(3-thiophene imine) ethylene (**B3TIE**) and N-octadecyl-3-thiophenylimine (**NOTPI**) monolayer (**ECP-SABM**) with Li_2PdCl_4 were enhanced more than that of without electrochemical polymerized monolayer (**SABM**),which was also proved that it is a universal rule for thiophene derivatives in this way.

Intrduction

Thiophene chemistry has been developed for a long time and is well established.[1] Polythiophenes are an important representative class of conjugated polymers,[2] among them, functional oligothiophenes have attracted comprehensive interest as π-conjugated materials.[3] Furthermore, novel molecular architectures having more complicated conjugated structures and sophisticated topologies have emerged as a consequence of increased versatility of thiophene chemistry and currently represent a most interesting and quickly spreading field of research, in which a large number of transition metal-containing polythiophens are of interest.[4]

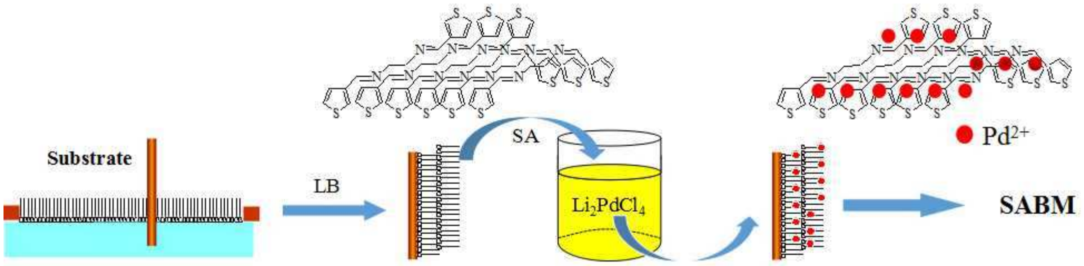
When the metal chelating units are incorporated to thiophenes or polythiophens, they show the electro-chromic behaviour of the polythiophene backbone, which is influenced by the coordinating metal center.[5] Palladium is one of the most utilized and versatile transition metals in modern synthetic organic chemistry, and the scope of palladium-mediated cross coupling reactions continues to broaden,[6] being commonly employed as bench test processes for new homo- and heterogeneous catalysts. Among of the metal complexes, Schiff based complexes are identified usually as building blocks of new conjugated polymers and supramolecular structures and have been used as materials for applications.[7] Umani-Ronchi, Wolf group et al. recently explored the use of oligothiophenes as versatile ligands for catalysts corresponding Pd complexes.[8] It is then of interest to construct model complexes in order to probe their interesting electronic properties and the catalytic activity by Wolf, M. O group, which show that the prepared cyclopalladated films are efficient in catalysing several cross-coupling reactions including the Suzuki-, Heck-, and Sonogashirain heterogeneous which is easily recovered and reused without loss of activity.[9]

Thiophene derivatives and their metal complexes films mentioned above prepared via self-assembly monolayers (SAMs) or Langmuir-Blodgett (LB) method which have attracted increasing interest during these years because they allow a straight forward preparation of chemically tailored surfaces with specific chemical and physical properties.[10] Among of which thiophene derivatives are adsorbed on Pt- or Au-surfaces or other substrates to form densely packed SAMs and subsequently electropolymerized. The resulting thin films show high electrochemical stability.[11] And at the same time, the application of Langmuir-Blodgett (LB) techniques to conjugated polymers offers a unique approach for constructing molecular devices and higher order thin films.[12] Organometallic catalytic LB films used for catalysis is first investigated by To¨ llner, K etc.[13] In our previous studies, we have synthesized a series of cyclopalladated ferrocenylimine (**CPFI**), which show satisfactory reactivity in Heck, Suzuki, Sonogashira and Kumada reactions etc. in homogenerous,[14] and also investigated molecule orientation and morphology of **CPFI** in LB films which clearly demonstrate that ordered structures have a major influence on a catalytic reaction.[15] However, the LB films may desorb from solid slides to some extent when it is placed in organic solvents or under heating conditions, which would affect the experiment results. Then cyclopalladated arylimine self-assembly films were synthesized to overcome these disadvantages.[16,17] which got better result that improved the catalytic activity and recycle ability. Although researches investigated above with self-assembly or LB technology for fabricating functional films have achieved excellent results, few investigation of order catalyst films fabricated by combining LB technology, electrochemical polymerization and self-assembly (called as **LB-ECP-SA**) is presented. Therefore, considering the special properties of thiophene unit, we designed and utilized the thiophene imine LB films electropolymerized to afford order packing of the metal oligopolymer trying to enhance the activity and reusability. To this purpose, we report here a relatively unexplored strategy to prepare high order monolayer of heterogeneous organometallic catalyst via self-assembly (**SA**) of electrochemical polymerized (**ECP**) Langmuir monolayer (**LB**) of **B3TIE** with Li_2PdCl_4 (called as **ECP-LB-SA**).

Given our background in palladacycles and the requirements for the successful incorporation of transition metals into thiophene or polychiophene, we designed a bis-Schiff base-type group linking dithiophene groups (See Scheme S1), in which the Schiff base system was ability to coordinate a broad range of transition metals.

Moreover, thiophene is an extremely well suited nucleus for special function, by leaving the more reactive 2- and 5-sites open, which is susceptible to electrochemical polymerization (**ECP**).[18]

Herein, 1,2-bis(3-thiophene imine)ethylene (**B3TIE**) and N-octadecyl-3-thiophenylimine (**NOTPI**) monolayer at water/air interface were characterized and can be transferred on to solid substrates to yield multilayers by Langmuir-Blodgett (LB) method. The **B3TIE** monolayer or electropolymerized **B3TIE** monolayer deposited on substrate was immersed in a solution of Li_2PdCl_4 to yield self-assembly palladacycle monolayer (**SABM**) which was shown in Scheme 1 and the palladacycle monolayer (**ECP-SABM**). It is worth note that the catalytic activity and recycle ability of **ECP-SABM** were enhanced more than that of **SABM** and **ECP-cast film**, indicating that ordered and orientation of molecular are the crucial factors for improving catalytic activity. The similar result was also observed in the case of **NOTPI**, indicating that there may be a universal rule for thiophene derivatives through this combination way (called as **LB-ECP-SA**). We attributed the higher catalytic activity to the order molecular packing, orientation and morphology to metal cheating with **B3TIE**, which is crucial in forming highly ordered, nanometersized domains with high density of active centre. These results represent a fundamental advancement in understanding the relationship between order, orientation and catalysis in heterogeneous and provide a general way to enhance the catalytic activity of thiophene-based palladium complexes for carbon-carbon coupling reaction.



Scheme 1 Schematic diagram of preparation of **SABM**.

Results and Discussion

Behavior and characterization of monolayer

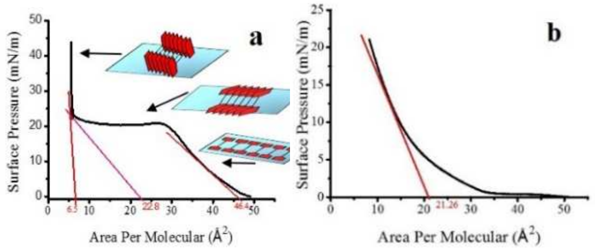


Figure 1. π–A isotherms of **B3TIE** (**a**) and **NOTPI** (**b**) obtained at 20 ºC. (Insets (**a**)): Orientation of **B3TIE** under investigation at three different surface pressures indicated by the arrows. Red dashed lines indicate the extrapolated area per repeat unit for the face-to (~46.4 Å^2), certain inclination angle (~22.8 Å^2) and vertical standing of (~6.5 Å^2) **B3TIE** orientations.

B3TIE is not an amphiphilic, hence not ideally suited to manipulation by the Langmuir technique. However, it was found that good Langmuir monolayer could be made by judicious choice of surface pressure (SP). The surface pressure rises at a moderate rate with decreasing area until a surface pressure of 21 mN/m is attained, at which point, the rate of increase in surface pressure with barrier compression a little decreases (Figure 1**a**). This plateau region of the isotherm continues until a surface pressure ~20 mN/m is reached. Further barrier compression leads to a much faster rate of surface pressure increase until evidence of film collapse appears beyond surface pressures > 45 mN/m.[19]

Analysis of the first increase in surface pressure showed that the area per repeat unit when extrapolated to zero pressure corresponds to ~46.4 Å^2, roughly two times larger than that of thiophene plane parallel to the water surface, in which the two thiophene in one molecular lies face to the water surface.[20,21] The shape of the isotherm of **B3TIE** is comparable to the reported by Groves, J. T etc.[22] At 25 mN m^{-1}, the mean molecular area is ~ 6.5 Å^2. This area is approximately half that of a single thiophene unit (14.5 Å^2), estimated for a close-packed monolayer with the dithiophene rings standing vertically to the air/water interface. On the other hand, **NOTPI** with an imine with alkyl chain in the repeat unit exhibit small surface areas (~21.26 Å^2) with relatively gradual increases in surface pressure without plateau region due to the hydrophobic function of chain, in which the thiophene plane face to interface and the alkyl chain expanded from interface (Fig.1**b**). These results indicate that an order packing monolayer could be achieved for both **NOTPI** and **B3TIE**.

Water contact angles changes (**WCA**)[23] and morphology of **B3TIE** monolayer deposited at different surface pressure (SP) on silicon were investigated with **WCA** and AFM shown in Figure 2, in which the water contact angles and surface configuration significant changed and meant that the **B3TIE** monolayer was successful transferred onto substrates.

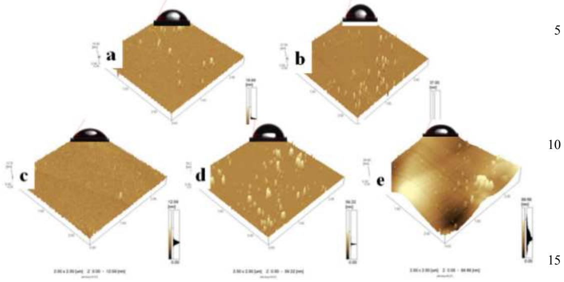


Figure 2 Water contact angles changes and AFM images (b) of **B3TIE** monolayer depositedon silicon at (a) 8 mN/m, (b) 10 mN/m, (c) 12 mN/m, (d) 14 mN/m and (e) 16 mN/m.(The roughness (a, 0.564 nm; b, 0,772 nm; c, 0.505nm; d, 1.78 nm; and e, 2.56 nm)

To gain some insight into the monolayer, electrochemical characterizations of **B3TIE** monolayer were performed. CVs of **B3TIE** monolayer on ITO at HCl compared to bare ITO are shown in **a** and **b** (see Fig. S1), respectively. Reduction peak of dithiophene imine at a potential of -0.2 to +0.3 V appeared, indicating that **B3TIE** monolayer was deposited. In the case of IR spectra, the special peak at around 1640 cm^{-1} which is designed to imine group was observed, indicating that the **B3TIE** monolayer was transferred onto substrate (Fig. S2).

Characterization and catalytic property of B3TIE self-assembly film

Catalytic property of self-assembly of **B3TIE** monolayer with Li$_2$PdCl$_4$ (**SABM**) was systematic investigated.The preparation of **SABM** was depicted in Scheme 1.

Characterization with WCAs and AFM of self-assembly of **B3TIE** monolayer indicated that the surface configuration had significant changed and that **SABM** was successful obtained (see Fig. S3, S4). To determine the conditions necessary to **SABM** and to verify that the self-assembly time employed here, AFM processed images of **SABM** were measured (see Fig. S5), in which different roughness were measured as 0.546 nm, 1.969 nm,3.021 nm,2.260 nm, 4.732 nm， for (a) 0h, (b) 24h, (c) 36h, (d) 48h, (e) 72h. There are some aggregating for 24h and 36h and extremely aggregation for 72h. Therefore, the best time was selected for 48 h due to its tendency toward the homo-packing.

The higher potential wave in CVs at about 0.94 V which is assigned to Pd^{2+} is irreversible (Fig. S6); Reduction peak of Pd^{2+}/Pd^{0} at a potential of 0.7 to 1.1 increased and shifted with increasing assembly time until 48h and decreased for 72h, indicating that **SABM** was completed for 48h. It is also worth noting that in the amplified parts from inset of Figure S6 in which the **B3TIE** peak at 0 to - 0.2V decreased quickly with increasing time and disappeared in 48h and then, appeared in 72h. It is also consistence with the results obtained above.

The peaks at 1637 cm-1 shifted to 1632 cm-1, 1628 cm-1, 1625cm-1 and 1632cm-1 while the intensity decreased with increasing self-assembly time (Fig. S7). The changes of special peak at 1632 cm^{-1} designed to imine group is the evidence that **SABM** was formed. The absorption of UV at 245 nm which is the cyclopalladated arylimine increased with increasing the self-assembly time, which is the evidence of **SABM** formation (Fig. S8). In the case of X-ray photoelectron spectroscopy (XPS) of **SABM**, a Pd (3d5/2), Pd (3d3/2) peak at 337.3 eV and 243.5 eV was observed, which is consistent with Pd(II) (no Pd(0) or (IV) was detected), indicating that **SABM** was fabricated (Fig.S9).The Pd content of the catalyst was 7.09×10^{-10} mol/cm^{2} detected by **ICP-AES** analysis, which is consistent with that calculated value.

Catalytic activity for Suzuki coupling reaction catalysed by **SABM** fabricated at different SP were investigated as shown in Table S1. The results showed that the best catalytic activity of **SABM** was determined at 12 mN/m, indicating that molecular orientation is one of the curial factor to catalyst[15b]. We also examined the reuse of **SABM** in Suzuki coupling reaction between 4-bromotoluene and phenyl boric acid under different conditions as shown in Table S2. Under the optimized conditions, the reaction of substrates extension were also investigated in detail (see Table S3).

Concerning the use of the catalyst both for industrial and pharmaceutical applications, the recycling was an important point. The inference of stirring and solvent were investigated (Fig. S10 (**a**)), in which high yield could be obtained without stirring (first times) and dramatic decreased in second due to the stirring which result in the catalyst being removed from the substrate. On the other hand, Recycling of **SABM** without stirring could be performed for four run (Figure S10(**b**)) without significant loss of catalytic activity (86%, 75% and 63% in sequence) (Table S4). It should also be noted that new phenomena might arise from the ability to organize catalysts into controlled assemblies to enhance the catalytic activity. At the meantime, changes in molecular design can also be used to improve their recycling ability compared to our previous research.[17]

In order to ascertain whether the catalysis is authentically heterogeneous, aliquots of liquid were removed from a Suzuki reaction run to completion from which the catalyst film had been removed, and a fresh K$_2$CO$_3$ mixture was added. In this case, the formation of only trace coupling product was observed (48 h reflux). This demonstrates that negligible activity results from leaching of catalyst from the films and that the catalysis is heterogeneous. Moreover, control experiments with the unmodified electrode (80 °C, 48 h, trace) showed that the support neither significantly affects the activity of **SABM** nor participates in the catalysis.

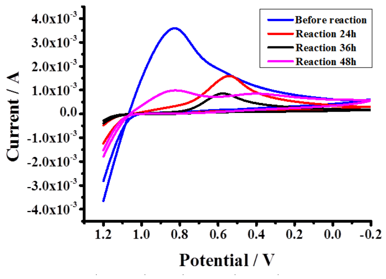


Figure 3 Cyclic voltammograms of **SABM** in the process of reaction

CV and AFM images of **SABM** on ITO after different catalytic time were taken to discuss the topographic and electrochemistry properties.

The curve of **SABM** acquired on ITO glasses had obvious difference after the catalytic reactions (Fig. 3). Reduction peak before catalysis was conspicuous from 0.7-1.0 V, which shifted to a range from 0.3 V to 0.75 V during reaction and the intensity decreased after catalysis. It indicated that the catalysts after catalytic reaction got harder to reduce and easier to oxidize, probably because the Pd catalysts had changed from oxidation state (Pd^{2+}) to reduction state (Pd^0). It suggested that Pd^0 was the catalytic activity center at the interface. It is interesting that the position of reduction peak restore to the initial state after 48 h although the intensity became weaker. It is plausible reason that the **SABM** were no more ordered or covered by the reagents which were obstacles for the current.

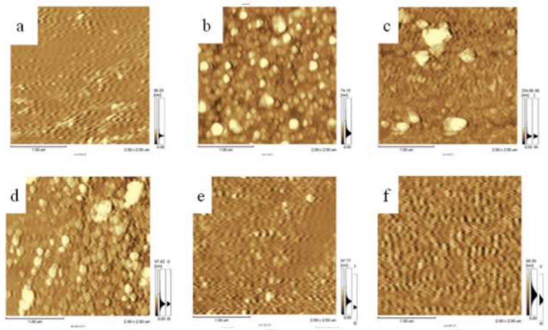


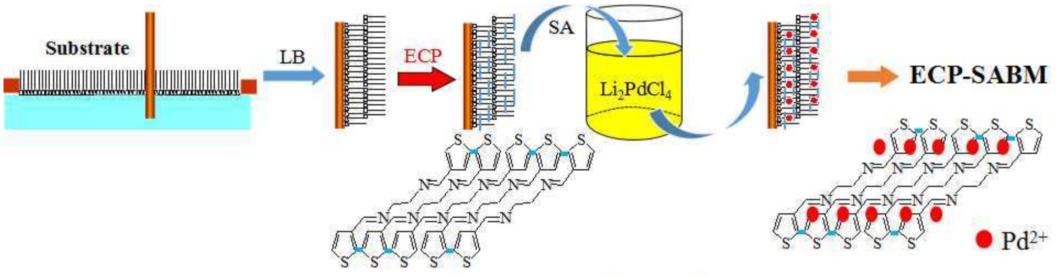
Figure 4 AFM images of **SABM** in the catalytic process of reaction acquired on silicon at (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 6 h, (e) 12 h, (f) 24 h

The AFM images of one-layer **SABM** acquired onto glass after different catalytic time were shown in Figure. 4. Smooth, order and uniform surface morphologies of **SABM** with rms (2.26 nm) was observed (Fig.S2d), in which the WCA were 64.9°. However, Figures 4a-e was the surface morphologies of **SABM** at different reaction time, in which remarkable morphological changes of catalyst film were detected. The confused aggregation phenomenon on the catalyst film surface with higher rms (35.5 nm, 27.7nm, 77.7nm, 25.5nm, 23.4nm) appeared (Fig. 4a-d) at about 0.5-6 hour catalysis, which revealed that the drastic catalytic process happened. Regio-uniform reappeared in Figure 3e (rms, 39.5nm) and homogeneous and order pattern were observed when the catalytic reaction was nearly completed (Fig.4f, rms, 45.7nm). The morphological changes of the catalyst films were remarkable, which could be illustrated by the surface changes made by the catalytic reaction. [24]

There was an interaction between the reactants and the support catalyst films which was consistent with previous studies.[25] It could be illustrated by the surface changes made by the catalytic active Pd on catalyst films.[26] These results indicated that **SABM** as heterogeneous catalyst to catalyse the coupling reaction proceeded via surface-catalyse process.

Catalytic properties of B3TIE fabricated with LB-ECP-SA way

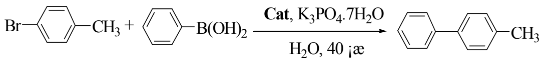
Catalytic activity of self-assembly Electrochemical polymerized **B3TIE** monolayer with Li_2PdCl_4 (called as **ECP-SABM**) was investigated (Scheme 2). The first electrochemical synthesis and their characterization as insoluble material were reported by Letheby.[27] Considering the advantage of **ECP** of thiophene oxidized state typically couple to yield oligomers or polymers and the solubility is often poor in solvents, we try to utility the electropolymerization of **B3TIE** Langmuir monolayer to form uniform polymer monolayer used to assembly with Li_2PdCl_4. It is expected to overcome the disadvantage of LB films as catalyst and enhance their catalytic activity as well as recycling.



Scheme 2 Schematic diagram of ECP-SABM

In this experiment, the key advantages stem from combining polymer synthesis and film formation into a single step, limiting the need for oxidants to initiate polymerization. Moreover, it is well-known that morphological control can be achieved through the employment of LB technologies and **ECP**. The thiophene oxidative dimerization of the molecule was confirmed at positive potentials.[28] Manipulation of electrochemical parameters, such as scanning run, can control oxidation states, yielding variable catalytic properties, while also controlling the local concentrations of incorporated metal at the polymeric interface which influence the local density at the interface. Therefore, optimization condition of scanning laps was investigated (Table 1). Scanning times for **B3TIE** monolayer on the ITO over the potential range 0-1.5 V results in oligomer film (**ECP-B3TIE**) and then **ECP-B3TIE** was immersed in a solution of Li_2PdCl_4 to yielded **ECP-SABM**. Catalytic activity of **ECP-SABM** was investigated, in which the **B3TIE** monolayer obtained after scanning 10 times over the complete potential range presented the highest catalytic property. The molecular weight of the electropolymeized monolayer (**ECP-SABM**) was also measured to be about 500 with GPC, indicating that mainly dimer was formed. So, scan runs were selected for next as shown in Table 1.

Table 1 Selection of scanning runs for Suzuki coupling reaction



Entry	Scanning laps	Isolated yield (%)	TON
1	5	43	8392
2	10	94	18345
3	15	73	14246
4	20	79	15417
5	25	84	16393
6	30	80	15613

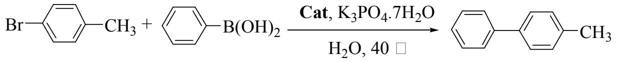
6 30 80 15613

Reaction condition: $PhB(OH)_2$ (0.30 mmol), 4-Bromotoluene (0.25 mmol), $K_3PO_4.7H_2O$ (0.30 mmol), H_2O (8 mL), TBAB (0.3mmol), 40℃ for 48 h. SP=12 mN/m

The key role played by **ECP-SABM** in a high level of catalytic activity was further evidenced by comparing with **SA** films analysis. Especially, orientation of **B3TIE** in monolayer electrochemical polymerized between the inner thiophene proved to be essential to create the stereochemical environment necessary to ensure high levels of chemical activity. Preparation of several catalysts films in different experiments (**Cat. ED-SABM, SABM, ECP-SABM, ECP-SABM**) was shown in Scheme 3 and their catalytic properties were exploited (Table 2). It is obvious that **ECP-SABM** has highest catalytic activity than that prepared in other methods, indicating that orientation of catalyst is one of the curial factor to catalysis. This method allowed the formation of nanometer size layers of **ECP-SABM** with normal orientation on the surface which can improve their catalytic activity.

Scheme 3 Fabrication of catalytic films via different route

Table 2 Data of catalysed Suzuki coupling reaction



Entry	^{a}Yields(%)	^{b}Yield(%)	TON
Cat. ED-SABM	23.8	30.0	5503
Cat. SABM	82.4	89.6	6726
Cat. ECP-SABM	94.0	>99.0	18345
Cat. SABM-ECP	31.4	39.2	7191

Reaction condition: $PhB(OH)_2$ (0.30 mmol), 4-Bromotoluene (0.25 mmol), $K_3PO_4.7H_2O$ (0.30 mmol), H_2O (8 mL), TBAB (0.3mmol), 40℃ for 48 h. a, Isolated yield , b. Yield determined by GC, based on the product.

Characterization of **ECP-SABM** has been examined by infrared, UV, XPS, AFM, Water contact angle as follow: Changes of WCA of hydrophilic substrate, **B3TIE** monolayer. **ECP-B3TIE** monolayer, **B3TIE** monolayer with Li_2PdCl_4 (**SABM**) and **ECP B3TIE** monolayer with Li_2PdCl_4 (**ECP-SABM**) were measured, in which various **WCA**s were induced by the changing of the properties of the surface (Fig. S11). The morphology of **B3TIE** monolayer, **ECP-B3TIE** monolayer, **SABM** and **ECP-SABM** on ITO surfaces were investigated (Fig. 4), in which **ECP-B3TIE** monolayer (c) generated regular Z-type linelike arrangement with low rms (5.6nm). In agreement with experimental results that thiophene only paralleled to the surface is favors coupling steps with neighboring monomer moieties.[29] Highly organized and closely packed Ziger-Ziger rodlike of **ECP-SABM** could be formed from **ECP-B3TIE** monolayer (e). However, in the case of **SABM**, region-regular orientation (d) was observed. These different arrangements would be easy to be controlled by direct **ECP** way,which will influence their catalytic activity. That is to say that the preorganization of a close-packed **B3TIE** monolayer prepared by LB method allows for the electrochemical generation of an order layer of the dimer that is highly organized and closely packed.

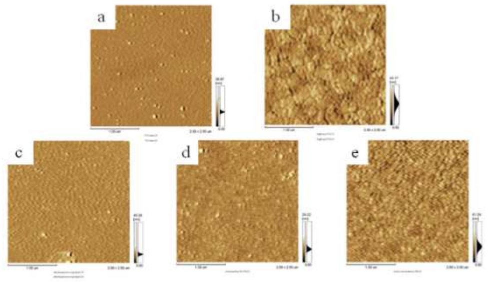


Figure 5 AFM images of (a) hydrophilic ITO ; (b) **B3TIE** monolayer ; (c) **ECP-B3TIE** monolayer ; (d) **SABM** and (e) **ECP-SABM**

CVs of (A) **SABM** and (B) **ECP-SABM** were presented in Figure 6. Compare to the CV of **SABM**, the voltammogram of (B) **ECP-SABM** showed reversible wave, in which contains a broad feature at lower potential assigned to reduction of Pd^0 (0.2-0.7V) and oxide peak at higher potential assigned to Pd^{2+} at range from 0.3-0.7V. It is possible that when the **ECP B3TIE** monolayer was put into Li_2PdCl_4 solution, most palladium were chelated into **ECP B3TIE** monolayer in the form of Pd^0 with the two nitrogen instead of cyclopalladated Pd^{2+} because that palladium is a strong transition metal binding ligand used to facilitate and control the assembly of molecular architectures, resulting the amount of Pd in **ECP-SABM** which is the half of **SABM** shown in Figure 4(B)**.** As we known that the active specie in initial process usually is Pd^0, it is the reason that the catalytic activity of **ECP-SABM** is higher than that of **SABM**.

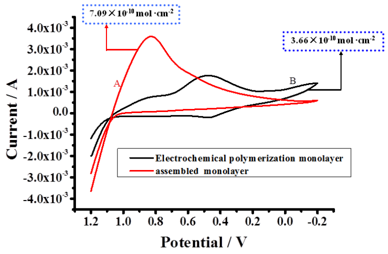


Figure 6 Cyclic voltammograms of **SABM** and **ECP-SABM**

Figure 7 presented the results of recycling of catalyst of **ECP-SABM** without stirring. Five runs were performed without significant loss of catalytic activity. The nice thing in these investigations was that new micro-phenomena of **ECP-SABM** might arise from the ability to organize molecular catalysts into controlled assemblies to enhance the catalytic activity and can also be used to improve their recycling ability compared to **SABM** because that the adhesive force with substrate of dimer is stronger than that of monomer. At meantime, it is also noted that the amount of Pd is a few loading[30], but high catalytic activity and recycling can be achieved with the combination way. Indeed, Pd chelated with **ECP-SABM** exhibited improved catalytic activity and stability. However, the structure of the catalyst in films was not clear, hindering to discuss catalytic mechanism. So, rational design of suitably catalysts should be closely linked to deeper insights into mechanisms involved at molecular level in future.

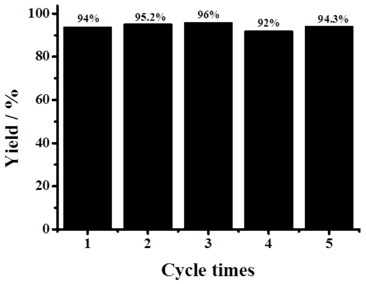


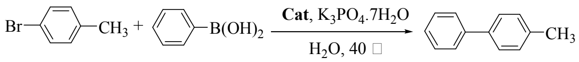
Figure 7 Yields obtained recycled catalyst of **ECP-SABM**

Contrast experimental

Combination of LB technology, **ECP**, and self-assembly (**called as LB-ECP-SA**), catalytic activity and recycle ability of **B3TIE** can be enhanced according to the results obtained above. That is to say that it is also possible to tailor the degree of molecular order by LB technology, to enhance mechanical property of films with **ECP** and chelate metal into certain form with molecular to afford a higher order packing of the metallic oligopolymer film which exhibits significantly catalytic property. In order to deeply prove it, other catalytic films prepared in different ways, such as self-assembly of **B3TIE** cast films with Li_2PdCl_4 (**SA-B3TIE-Cast**), self-assembly of electrochemical polymerized **B3TIE** cast films with Li_2PdCl_4(**SA-ECP-B3TIE-Cast**), were designed and the results obtained presented in Table 3, in which orientation of molecular and fabrication are very important for higher catalytic activity.

Whether or not the combination used in present research is universal prepared in various ways.

Table 3 Data of Suzuki coupling reaction catalyzed by **B3TIE** films

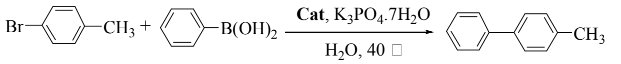


Entry	Isolated Yield（%）	TON
SA-B3TIE-Cast	47.5	3877
SA-ECP-B3TIE-Cast	62.1	5069
SABM	82.4	6726
ECP-SABM	94.5	18345

Reaction condition: $PhB(OH)_2$ (0.30 mmol), 4-Bromotoluene (0.25 mmol), $K_3PO_4.7H_2O$ (0.30 mmol), H_2O (8 mL), TBAB (0.3mmol), 40℃ for 48 h.

for compounds containing thiophene group. **NOTPI** LB films were prepared at different SP, followed by self-assembling with Li_2PdCl_4 (**SANOTPI**) or by **ECP** process and then self-assembling with Li_2PdCl_4 (**ECP-NOTPI**). The data were presented in Table 4. The results also showed that not only the orientation of **NOTPI** in film but also the **ECP** technology play an important role for improving catalytic activity. Such a combination system used for thiophene-based compounds shows a model for improving catalytic activity, with which we can expand the functionality of the modified surface and provide new insights into the heterogeneous catalyst.

Table 4 Catalytic property of **SANOTPI** fabricated at different SP (entry 1-3) and **ECP-NOTPI** (entry 4).



Entry	SP (mN/m)	Isolated Yield (%)	TON
1	9	24	1959
2	11	55	4489
3	13	17	571
4	11	72	10253

Reaction condition: $PhB(OH)_2$ (0.30 mmol), 4-Bromotoluene (0.25 mmol), $K_3PO_4.7H_2O$ (0.30 mmol), H_2O (8 mL), TBAB (0.3mmol), 40℃ for 48 h.

Conclusion

1,2-bis(3-thiophene imine)ethylene (**B3TIE**) and N-octadecyl-3-thiophenylimine (**NOTPI**) monolayer at water/air interface were characterized and can be transferred on to solid substrates to yield multilayers by Langmuir-Blodgett (LB) method. The **B3TIE** monolayer or electropolymerized **B3TIE** monolayer deposited on substrate was immersed in a solution of Li_2PdCl_4 to yield self-assembly palladacycle monolayer (**SABM**) and the palladacycle monolayer (**ECP-SABM**). It is worth note that the catalytic activity and recycle ability of **ECP-SABM** were enhanced more than that of **SABM** and **ECP-cast film**, indicating that ordered and orientation of molecular are the crucial factors for improving catalytic activity. The similar result was also observed in the case of **NOTPI**, indicating that there may be a universal rule for thiophene derivatives through this combination way (called as **LB-ECP-SA**). We attributed the higher catalytic activity to the order molecular packing, orientation and morphology to metal cheating with **B3TIE**, which is crucial in forming highly ordered, nanometersized domains with high density of active centre. These results represent a fundamental advancement in understanding the relationship between order, orientation and catalysis in heterogeneous and provide a general way to enhance the catalytic activity of thiophene-based palladium complexes for carbon-carbon coupling reaction.

Experimental Section

General

All solvents were obtained from commercial sources and used without purification. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα 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. Cyclic Voltammetry (CV) curves were obtained by CH 1650A,Experiments were performed in three electrodes cells in 0.5 M HCl. The counter electrode was platinum; the reference electrode was Ag/AgCl/(0.1M)KCl. All the Suzuki reaction was accomplished without the protection of inert gas. HPLC was conducted on a Waters 600 liquid chromatograph. Atomic Absorption Spectroscopy (AAS) analysis was obtained by Z-8000 polarized Zeeman atomic absorption spectrophotometer (Hitachi Corporation, Japan). Melting points were measured using a WC-1 microscopic apparatus and are reported were uncorrected. C, H, and N analyses were performed on a FLASH EA1112 analyzer. Infrared spectra were recorded on a Bruker VECTOR22 spectro-photometer.^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl3 with TMS as an internal standard. Mass spectral data were acquired on an LC-MSD-Trap-XCT instrument. UV-visible absorption spectrum was obtained on Lambda 35 UV-Visible spectrophotometer (Perkin Elmer Inc. USA). The molecular weight was determined with PL-GPC 50 in tetrahytdrofuran (THF) with polystyrene standards. Measurement of surface pressure (π)-area(A) isotherms and the deposition of monolayer were carried out with a computer controlled Langmuir trough Langmuir -Blodgett system (KSV-5000-3, KSV Instruments, Helsinki, Finland) .Water contact angle is measured on an HARKE-SPCX1 instrument(Bejingjing).

General synthesis process for NOTPI, B3TIE (Scheme S1)

In a 50 mL flask, mixture of alkylamine or alkyldiamine or 3-Thiophenaldehyde (6 mmol), MgSO4 (15 mmol), 600 □L of 3-Thiophenaldehyde and *p*-Toluenesulfonic acid dissolved in 30 mL of CH_2Cl_2 was added. The mixture was stirred at room temperature for 48 h under nitrogen. The mixture was then filtered through column with diatomite and the solvent was removed under reduced pressure. The residue was dissolved with proper amount dichloromethane again and methanol was added. The product was obtained by filteration, washed with methanol and dried under vacuum.

N-octadecyl-3-thiophenylimine (**NOTPI**): white solid, mp: 45.8-46.3 ℃. Yield, 83%. IR (KBr, Pellet) (cm^{-1}): 3059, 2918, 1615, 1502, 1447, 1367, 1257, 831. MS: 364 $[M+H]^+$. ^{1}HNMR (400 MHz, $CDCl_3$): δ(ppm)=8.18 (1H, s, -CH=N-), 7.46 (2H, m, -CH-S-CH-), 7.2 (1H, s, -CH-CH-S-), 1.21 (34H, d, J=8.1Hz, CH_3-$(CH_2)_{16}$-CH_2), 0.80 (3H, t, CH_3-). ^{13}CNMR (100 MHz, $CDCl_3$): δ(ppm)=154.11, 139.55, 126.99, 125.29, 124.75, 60.78, 28.69, 28.44, 28.36, 26.32, 21.68, 13.11.

1,2-bis(3-thiophene imine)ethylene (**B3TIE**): brown solid, m.p: 91.8-91.9 ℃, Yield, 52%. IR (KBr, Pellet): 3047, 2919, 2848, 1711, 1638, 1420, 825, 714cm^{-1}. MS: 248.9 [M+H]$^{+}$. ^{1}HNMR (400MHz, $CDCl_3$): δ(ppm)=8.29 (2H, s, -CH=N-), 7.54 (4H, m, -CH-S-CH-), 7.30 (2H, m, -CH-CH-S-), 3.91 (4H, s, $-CH_2-N=$). ^{13}CNMR (100MHz, $CDCl_3$): δ(ppm)=156.0, 139.42, 127.49, 125.37, 124.68, 60.68. Cyclopalladated dithiophendiimme (**CPDTDI**) were prepared as follow: A mixture of Li_2PdCl_4 (1.0 mmol), sodium acetate (1.0 mmol), thiophenediimine (1.1 mmol) in methanol (10 ml) was stirred for 24 h with ice bath, then filtered and washed with ethanol. Yellowshi products were obtained and purified in chromatograph with dichloromethane and ethanol (2:1) as eluent. Mp：>300 ℃.

Suzuki cross-coupling reactions

Aryl halide (0.25 mmol), aryl boric acid (0.3 mmol), catalyst (0.1 mmol %) and TBAB (0.3 mmol) were combined with base (0.3 mmol) and deionized water (1.5 mL) in a small round-bottom flask. The reaction mixture was stirred and then extracted with ethyl acetate for three times. The combined organic phase was dried with $MgSO_4$, filtered, and the solvent was analyzed by gas chromatography.

Self-assembly of dithiophene derivatives monolayer with Li_2PdCl_4

The thiophene derivatives monolayer deposited on substrates were put into a solution of Li_2PdCl_4 for certain time and then taken out, washed with methanol for several times.

Preparation of the Langmuir monolayer and LB films

Spreading solution of palladacycles was carefully spread onto the ultrapure water surface, and the Langmuir monolayer was compressed after evaporation of solvent (all the solvent was chloroform) for 30 min and stabilization for ca. 1 h in the uncompressed state at a compression speed of 5 mm/min at 20±1 ºC. LB films were transferred onto ITO glasses (for electrochemical study), quartz (for UV studies) and silicon slides (for AFM instruments and catalysis study). The silicon, quartz and glass slides were cleaned in boiling concentrated H_2SO_4 for 1 h and then washed with pure water. The ITO glasses were ultrasonic washed in acetone, ammonia, ethanol and pure water in sequence.

Hydrophilic treatment

The silicon and glass wafers were put into the mixed solvent of concentrated nitric acid and concentrated sulphuric acid (v:v=2:1) and heated to boiling for 1-1.5h. Then, the wafers were washed by amount of deionized water. The ITO glasses were ultrasonic washed in acetone, ammonia, ethanol and pure water in sequence.

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis

After the reaction was over, the wafer was removed and the reaction mixture was centrifuged and broken down with nitrolysis, in which the Pd concentration was measured by ICP-AES.

Recovery and reuse of the modified ITO electrode in Suzuki reaction

Optimal reaction conditions were employed for each run. The electrode was then removed from the reactor, washed with methanol, dried under vacuum and reused without further purifications.

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Keywords: Cyclopalladated thiophene imine; self-assembly;
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1 Gronowitz, S.; Ho¨rnfeldt, A.B, Elsevier Academic Press: San Diego, CA, **2004**.

2 a) Beaujuge, P. M.; Fréchet, J. M. J. J. Am. Chem. Soc. **2011**, 133, 20009; b) Julia A. Schneider, AfshinDadvand, Wen Wen, and Dmitrii F. Perepichka, Macromolecules **2013**, 46, 9231; c) Weiwei Li, Koen H. Hendriks, Alice Furlan, W. S. Christian Roelofs, Martijn M. Wienk, and René A. J. Janssen, *J. Am. Chem. Soc.*, **2013**, *135* (50), 18942; d) Tomohiro Shiraki, Arnab Dawn, Youichi Tsuchiya, and Seiji Shinkai,*J. Am. Chem. Soc.*, **2010**, *132* (39), 13928

3 a) Amaresh Mishra, Chang-Qi Ma, and Peter Ba¨uerle, *Chem. Rev.* 2009, *109,* 1141; b) Antonio Facchetti, Melissa Mushrush, Myung-Han Yoon, Geoffrey R. Hutchison, Mark A. Ratner, and Tobin J. Marks, *J. Am. Chem. Soc.*, **2004**, *126* (42), 13859; c) B. Vercelli and G. Zotti , A. Berlin , M. Pasini and C. Botta , R. Gerbasi , T. L. Nelson and R. D. McCullough, *J. Phys. Chem. C*, **2012**, *116* (2), 2033; d) Michael T. Otley, Fahad Alhashmi Alamer, Yumin Zhu, Ashwin Singhaviranon, Xiaozheng Zhang, Mengfang Li, Amrita Kumar, and Gregory A. Sotzing, *ACS Appl. Mater. Interfaces*, **2014**, *6* (3), 1734

4 a) Benjamin W. Maynor, Shaun F. Filocamo, Mark W. Grinstaff, and Jie Liu, J. Am. Chem. Soc, **2002**, 124(4), 522

5 a) Jerry L. Reddinger and John R. Reynolds, Reddinger, J. L.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 3; b) Julien Boixel,Véronique Guerchais, Hubert Le Bozec, Denis Jacquemin, Anissa Amar, Abdou Boucekkine, Alessia olombo, Claudia Dragonetti, Daniele Marinotto, Dominique Roberto,Stefania Righetto,and Roberta De Angelis, J. Am. Chem. Soc. **2014**, 136, 5367; c) Richard P. Kingsborough and Timothy M. Swager, *J. Am. Chem. Soc.* **1999**, *121,* 8825; d) Alfred C. W. Leung, Jonathan H. Chong, Brian O. Patrick, and Mark J. MacLachlan， *Macromolecules* **2003**, *36,* 5051 ;

6 a) Suzuki, A. *Chem. Commun.* **2005**, 4759

7 a) Kim, D. H.; Cho, H. I.; Zyung, T.; Do, L.-M.; Bark, K.-M.; Shin, G. C.; Shin, S. C. *Eur. Polym. J.* **2002**, *38*, 133; b) Zhang, H. C.; Huang, W. S.; Pu, L.*J. Org. Chem.* 2001, *66*,481; c) Richard P. Kingsborough and Timothy M. Swager, *J. Am. Chem. Soc.*, **1999**, *121*(38), 8825.

8 a) Albano, V. G.; Bandini, M.; Barbarella, G.; Melucci, M.; Monari,M.; Piccinelli, F.; Tommasi, S.; Umani-Ronchi, A. *Chem.Eur. J.* **2006**, *12*, 667; b) Mucci, A.; Parenti, F.; Pigani, L.; Seeber, R.; Zanardi, C.; Pilo,M. I.; Spano, N.; Manassero, M. *J. Mater. Chem.* **2003**, *13*, 1287; c) Clot, O.; Wolf, M. O.; Patrick, B. O. *J. Am. Chem. Soc.* **2001**, *123*, 9963.

9 a) Albano, V. G.; Bandini, M.; Moorlag, C.; Piccinelli, F.; Pietrangelo, A.; Tommasi, S.; Umani-Ronchi, A.; Wolf, M. O. *Organometallics* **2007**, *26*, 4373

10 a) C. Nogues, P. Lang, B. Desbat, T. Buffeteau and L. Leiserowitz, *Langmuir*, **2008**, *24* (16), 8458; b) Ocafrain, M.; Tran, T. K.; Blanchard, P.; Roncali, J. *Adv. Funct. Mater.* **2008**, *18*, 2163; c) Wolf, M. O. *Adv. Mater*. 2001, *13*, 545;Joachim Engelking, Dagmar Ulbrich, and Henning Menzel *Macromolecules*, **2000**, *33* (24), 9026

11 a) Heejoon Ahn, Myunghwan Kim, Daniel J. Sandman, and James E. Whitten, *Langmuir*, **2003**, *19* (13), 5303; b) Lei Zhang, Nicholas S. Colella,Feng Liu,Stephan Trahan,Jayanta K. Baral,H. Henning Winter,Stefan C. B. Mannsfeld, and Alejandro L. Briseno, J. Am. Chem. Soc. **2013**, 135, 844; c) Yoko Tatewaki, Yuki Noda, Tomoyuki Akutagawa, Ryo Tunashima, Shin-ichiroNoro, Takayoshi Nakamura, Hiroyuki Hasegawa, ShinroMashiko, and Jan Becher*J. Phys. Chem. C*, **2007**, *111* (51), 18871

12 a) Yuko Takeoka, Fumihiko Saito, and Masahiro Rikukawa *Langmuir*, **2013**, *29* (27), 8718; b) Mariane Perpethue Ouattara, Stéphane Lenfant, Dominique Vuillaume, Michel Pézolet, Jean-François Rioux-Dubé, JoséeBrisson, and Mario Leclerc *Macromolecules*, **2013**, *46* (16), 6408; c) Jusroop S. Mattu and Gary W. Leach， *J. Am. Chem. Soc.*, **2010**, *132* (9), 3204

13 a) To¨ llner, K.; Popovitz-Biro, R.; Lahav, M.; Milstein, D. Science **1997**, 278, 2100; b) Benı´tez, I. O.; Bujoli, B.; Camus, L. J.; c) Lee, C. M.; Odobel, F.; Talham, D. R. *J. Am. Chem. Soc.* 2002, 124

14 a) G.Z Ma,Y.T Leng , Y.S Wu , Y.J Wu, *Tetrahedron*, **2013**, 69, 902; K. Xu, F.Yang; G.D Zhang; Y.J Wu, Green Chemistry, **2013**, 15(4), 1055; b) X. Li, ; F.Yang; Y.J Wu, Journal of Organic Chemistry, **2013**, 78(9), 4543; c) Mu B, Li T S, Li J Y, Wu Y J. *J Organomet Chem,* **2008**, 693: 1243; d) Mu B, Li T S, Fu Z H, Wu Y J. *Catal Commun,* **2009**, 10: 1497; e) Y. Li, Z.H Fu, L. Rao, L. Wang, R. Li, T. Li, Y. Wu, *J. Chin. Chem. Soc.* **2014**, *61*, 397; f) X. Mi, M.M Huang, J. Zhang, C. Wang, and Y.J Wu, Organic Letters, **2013**, 15 (24), 6266; g) X.J Li, D.P Zou, F.Q Leng, C.X Sun, J.Y Li, Y.J Wu, Y.S Wu, *Chem. Commun*., **2013**, 49, 312

15 (a) Z. Fu, T. Li, B. Mu, L. Mao, G. Li, W. Xu, Y. Wu, *J. Mol. Catal. A: Chem.*, **2012**, 200,363; (b) B. Mu, T. Li, C. Li, P. Liu, W. Shang, Y. Wu, *Tetrahedron,* **2009**, 65, 2599.

16 a) T. Li, Z. Zhai, J. Qiu, W Xu, H. Liu, Y. Wu, *ChemCatChem*., **2013**, 5, 1481; b) Zhihua Fu, Na Zhang, T.S Li, W.J Xu, Y.J Wu, Journal of Colloid And Interface Science, **2013**,394,409; c) Z.H Fu, J. Liu, X.H He, T.S Li, Y.J Wu˒ *RSC Advance*, **2014**, 4 (50), 26413

17 a) N. Zhai, F. Wang, M.L Zhou, T.S Li , H. Liu, W.J Xu, Y.J Wu, *Chinese Journal of Catalysis* **2013**, 34 (8): 1583

18 a) J. L. Reddinger, J. R. Reynolds, Chem. Mater. 1998, 10, 1236.

19 a) Jusroop S. Mattu and Gary W. Leach *J. Am. Chem. Soc.* **2010**, *132*, 3204

20 a) Callender, C. L.; Carere, C. A.; Daoust, G.; Leclerc, M. *Thin Solid Films* **1991**, *204* (2), 451

21 a) J. Mattu, T. Johansson, S. Holdcroft, and G. W. Leach *J. Phys. Chem. B* **2006**, *110,* 15328

22 a) Xu, G.; Bao, Z.; Groves, J. T. *Langmuir* **2000**, *16*, 1834

23 a) J. S. Sharp, D. J. Farmer and J. Kelly, *Langmuir* **2011**, 27, 9367.

24 a) F. Y. Zhao, M. Shirai, Y. Ikushima and M. Arai, *J. Mol. Catal. A: Chem*, **2002**, 180, 211

25 a) P. J. Ellis, I. J. S. Fairlamb, S. F. J. Hackett, K. Wilson, A. F. Lee, *Angew. Chem. Int. Ed.*, **2010**, 49, 1820

26 a) C. Copéret, M. Chabanas, R. Petroff Saint-Arroman and J-M. Basset, *Angew. Chem. Int. Ed.*, **2003**, 42, 156; b) X. Huang, Y. Li, Y. Chen, E. Zhou, Y. Xu, H. Zhou, X. Duan,and Y. Huang *Angew. Chem. Int. Ed.*, **2013**, 52, 2520

27 a) Letheby, H. *J. Am. Chem. Soc.* 1862, *15*, 161; Ju¨rgenHeinze, Bernardo A. Frontana-Uribe,and Sabine Ludwigs， *Chem. Rev.* **2010**, *110,* 4724

28 a) Chung, Jeff L. Shepherd, Dan Bizzotto, and Michael O. Wolf, *Langmuir* **2004**, *20,* 8270

29 a) Berlin, A.; Zotti, G.; Schiavon, G.; Zecchin, S. *J. Am. Chem. Soc.***1998**, *120*, 13453

30 a) S D Walker, T E Barder, J R Martinelli, S L Buchwald, *Angew Chem Int Ed.* 2004, 43, 1871; b) M R Biscoe ,B P Fors ,S L Buchwald . *J Am Chem Soc*. **2011**, 133, 16707; c) B P Fors, D A Watson, M R Biscoe, S L Buchwald. *J Am Chem Soc*. **2008**, 130, 13552; d) T E Barder, S D Walker, J R Martinelli, S L Buchwald. *J. Am. Chem. Soc.*, **2005**, 127, 4685.