Table 2. Pb(0)-catalyzed coupling reaction of allyl N-acyl-N-tosylimide (2b, 2c)

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Nucleophile</th>
<th>Reaction condition</th>
<th>Products &amp; yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pivaloyl</td>
<td></td>
<td>20°C, 3.5 h</td>
<td>![N-Ts] + POM(0) → Na + Products</td>
</tr>
<tr>
<td>2</td>
<td>Pivaloyl</td>
<td></td>
<td>20°C, 4 h</td>
<td>![N-Ts] + POM(0) → Na + Products</td>
</tr>
<tr>
<td>3</td>
<td>Pivaloyl</td>
<td></td>
<td>20°C, 10 min</td>
<td>![N-Ts] + POM(0) → Na + Products</td>
</tr>
<tr>
<td>4</td>
<td>Pivaloyl</td>
<td></td>
<td>20°C, 11 h</td>
<td>![N-Ts] + POM(0) → Na + Products</td>
</tr>
<tr>
<td>5</td>
<td>Pivaloyl</td>
<td></td>
<td>20°C, 11 h</td>
<td>![N-Ts] + POM(0) → Na + Products</td>
</tr>
<tr>
<td>6</td>
<td>Pivaloyl</td>
<td></td>
<td>20°C, 10 min</td>
<td>![N-Ts] + POM(0) → Na + Products</td>
</tr>
</tbody>
</table>

*All yields are isolated ones.

References


Formation of Self-assembled Zirconium N,N'-Bis (benzyl phosphonic acid)-3,4,9,10-perylene(dicarboximide) Multilayer Films on Silicon Substrate

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Self-assembled mono- and multilayer formed on solid substrates have generated considerable interest because of the potential of controlling the molecular architecture and chemical and physical properties of layered assemblies on surfaces such as electron transfer, nonlinear optics, photocatalysis, molecular recognition. Researchers have utilized the transition metal phosphonates multilayer films on surfaces to study a system in which interlayer distance and orientation of the organic components are crucial. The metal phosphate films provide an attractive means of constructing thermally and sovolytically stable films of controlled thickness, which consist of spatially well-defined molecular components. In this communication, we report on the preparation of multilayer of zirconium N,N'-bis(benzyl phosphonic acid)-3,4,9,10-perylene(dicarboximide)(Zr-BPPI) based on the sequential adsorption of metal ion and bisphosphonic acid and on the characterization of the multilayer structure using UV-visible absorption measurement, ellipsometry, and cyclic voltammetry. The perylenedicarboximide derivatives have been well known as photoconducting materials in xerography and as photoinduced electron transporting materials. The photo conductivity of the BPPI comes from the strong π-π interactions between fused aromatic ring structures. One of the goals of our research is to incorporate photoactive BPPI molecules into multilayer assemblies, in order to prepare thin films which undergo efficient photoinduced charge separation and directional conductivity.

In the multilayer structure of Zr-BPPI presented here the adjacent perylene chromophore in each layer can be stacked each other perpendicularly to the substrate as shown sche-
matically in Figure 2. BPPI was prepared from the condensation reaction of 3,4,9,10-perylenedicarboxylic dianhydride and 4-amino benzyl phosphonic acid, which is prepared from acid hydrolysis of diethyl 4-aminobenzyl phosphonate, in a molten imidazol with zinc acetate at 170 °C. BPPI was confirmed from IR absorption peaks. The absorption peak, 1774 cm⁻¹ of CO in dianhydride has been changed to 1701 and 1661 cm⁻¹ of CO in imide. The BPPI is not soluble in any other solvents except in H₂O. But since the compound exists as a dimer due to the strong aromatic ring interaction, the NMR spectrum in D₂O was very broad and not discernible. Zr-BPPI films were grown using a methodology developed by Katz. The cleaned silicon substrate was rinsed with acetonitrile and then phosphorylated by treatment with an acetonitrile solution of POCl₃ and 2,4,6-collidine (10 mM in each) for 12 h at 80 °C. The substrates were zirconated in a 5 mM solution of ZrOCl₂ for 3 h at room temperature. Multilayers of Zr-BPPI were produced by alternate dippings in 5 mM BPPI and ZrOCl₂ solution at room temperature for 1 h. Films were thoroughly rinsed with deionized water between dippings.

The UV spectra of Zr-BPPI multilayer films on quartz plate displayed a strong absorbance at 500 nm and 542 nm and those of BPPI solution exhibits a strong absorption band at 508 nm. This results indicates that the Zr-BPPI films is grown uniformly by the effective π-π interactions among inter- and intramolecules. Figure 3 shows the UV absorbance at 500 nm as a function of the number of layer of Zr-BPPI films on a quartz plate.

As the number of layer increased, the absorbance of the film increased linearly. Figure 4 shows the thickness of BPPI multilayer films as a function of the number of layer. Under the assumption that the Zr-BPPI layer has the same refractive index of Zr-decanesphosphonate layer, the average thickness of layer was determined. In the plot of the number of layer vs thickness, the slope of the line related to the average thickness of layer is 15.8 Å/layer. The straight-line indicates that individual layer is uniformly grown in average thickness.

The multilayers of Zr-BPPI can be grown on the nanoporous particulate films as well as planar substrates such as silicon and quartz. Figure 5 shows cyclic voltammograms of BPPI layers on nanoporous TiO₂ film electrode. The quasi-reversible peak currents are systematically increased as the number of layer increases although the cathodic peaks are higher than anodic ones. The reason for the difference is not clear at this point. Control experiments showed that the redox peak currents do not increase without treatment of zirconyl chloride solution in each layer-growing step. As the layers grow, the integrated charges of cathodic peaks after background subtraction are almost linearly increased (not shown here).

It shows that the adsorbate concentration in each layer is pretty constant. Since the absorption spectrum of BPPI is different from the reduced BPPI, we are currently investigating the possibility of electrochromic device using these...

Figure 5. Cyclic voltammogram of BPPI layer on TiO2.

redox couple multilayer. Although UV spectra, ellipsometric measurements, and cyclic voltammogram suggest that the Zr-BPPI films grow uniformly, the atomic images of multilayer films are needed to confirm the uniformity of films. Therefore, the AFM measurement of Zr-BPPI films is being carried out to study film uniformity and growth on a microscopic level.

In summary, it is shown that the layer thickness measured by ellipsometry linearly increases as a function of the number of layer deposited and UV-vis spectroscopic results of the deposition process are consistent with those of ellipsometric measurements. The average thickness of the film derived by ellipsometry was observed about 15.8 Å. Also, according to cyclic voltamogram, the quasi-reversible peak currents are systematically increased as the number of layer increases. These results indicate that the same amount of BPPI layer is placed on the substrate after each deposition cycle.

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References


Kinetic Analysis of Inactivation of the cdc25 Phosphatase by Menadione

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Cdc25 phosphatases catalyze tyrosine-15 dephosphorylation of the p34cdc2, catalytic subunit of the M phase-Promoting Factor (MPF),1,2 this leads to the G2/M transition of the cell cycle in all organisms.3,4 These enzymes play an important role in the regulation of cell division cycle and present a promising target for the design of potential chemotherapeutic agents in the field of antitumor treatment.5-7 Since it has been reported that menadione induced alterations in the phosphorylation status and the activity of protein tyrosine phosphatase,8 and menadione shares a enone structure with some mechanism-based inhibitors of phosphatases that have been previously reported,9,10 we have re

11. Nanoporous TiO2 film electrode was prepared using Degussa P25 TiO2 by the method of Graetzel et al’s12. The thickness of the TiO2 film is about 4 µm estimated from SEM picture. The geometric area of the electrode is 1.5 cm2. However the actual surface area of the TiO2 electrode is about 1000 times higher than that considering nanoporous nature. The cyclic voltammograms were measured in three cell electrode system with Pt counter and SCE reference electrode. The electrolyte solution was 0.1 M KCl and the scan rate was 25 mV/sec. The detail electrochemical studies of these multilayers on the TiO2 electrode will be presented in the other paper.