

Swellable Submicrospheres of Ionic Palladium(II) Complexes Containing Decylmethylbis(*m*-pyridyl)silane

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Received July 15, 2009, Accepted September 2, 2009

Ionic palladium(II) complex containing a long aliphatic chain, [(tmeda)PdL]₂(PF₆)₄ (tmeda = *N,N,N',N'*-tetramethylethylenediamine; L = decylmethylbis(*m*-pyridyl)silane) allowed to form a puckered submicrosphere morphology without any template or additive. The puckered spheres reversibly adsorb and desorb dioxane molecules. Coligand and cosolvent effects on the formation of submicrospherical morphology were observed.

Key Words: Coligand effects, Decylmethylbis(*m*-pyridyl)silane, Ionic palladium(II) complexes, Swellable submicrospheres

Introduction

The formation and modification of specific submicro morphology by means of chemical perturbations is of central importance in development of unique functional submicromaterials.¹⁻⁸ A unique morphology from molecular building blocks promises to provide task-specific properties such as photo-electronic devices, pigments, ion exchangers, desiccants, molecular recognizers, drug delivery chemicals, biomimetics, cosmetics, chromatographic materials, and catalysts.⁹⁻¹⁶ Facile methods for the formation and tuning of submicrospherical morphology *via* surface tension, capillary effects, electric and magnetic forces, and hydrophilic interactions have been highly desired.¹⁷⁻²³ Thus, the size-control of submicrospheres using ionic metal complexes is one of the most important issues,^{6,24,25} but the formation and applications of swellable submicrospheres are rare.²⁶ In this context, the formation of swellable submicrospheres of ionic metal complexes containing a long chain aliphatic organic group along with their solvent-adsorption and desorption will be reported. Formation of the microspheres was carried out by the reaction of (N-N)Pd(PF₆)₂ (N-N: *N,N,N',N'*-tetramethylethylenediamine = tmeda; ethylenediamine = en; 2,2'-bipyridine = bpy) with decylmethylbis(*m*-pyridyl)silane (L) with a new long hydrophobic aliphatic chain. Furthermore, the palladium(II) chemistry can be attributed to catalysis and dual characters.^{27,28}

Experimental

Materials and Measurements. Potassium tetrachloropalladate (K₂PdCl₄), *N,N,N',N'*-tetramethylethylenediamine (tmeda), ethylenediamine (en), 2,2'-bipyridine (bpy), and AgPF₆ were purchased from Aldrich, and used without further purification. Decylmethylbis(*m*-pyridyl)silane (L) was prepared by a method outlined in our previous literatures.²⁹ ¹H NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz, and the chemical shifts were relative to the internal Me₄Si. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer with samples prepared as KBr pellet. Elemental microanalyses (C, H, N) were performed on solid samples by the

Advanced Analytical Division at Pusan Center, KBSI using a Vario-EL III. Thermal analyses were performed under a nitrogen atmosphere at a scan rate of 10 °C/min with a Labsys TGA-DSC 1600. Mass spectrometric analysis was performed in chloroform by KMS-700 Mstation Mass Spectrometer (Jeol, Japan) using a MS-MP9020D data system. Scanning electron microscopic images were obtained on a JEM 2011.

[(tmeda)PdL]₂(PF₆)₄. L (0.1 mmol, 34 mg) in 10 mL of acetone was added slowly to (tmeda)Pd(PF₆)₂ (0.1 mmol, 51 mg) in 10 mL of distilled water. The mixture was refluxed for 5 h, and slow evaporation of acetone at ambient temperature produced a white product in a 70% yield. Anal. Calcd for C₅₄H₉₆N₈F₂₄P₄Pd₂Si₂: C, 38.01; H, 5.67; N, 6.57. Found: C, 37.20; H, 5.52; N, 6.50. ¹H NMR (300 MHz, CD₃CN, Me₄Si): δ 0.60 (s, 6H), 0.88 (s, 4H), 2.54 (s, 24H), 2.92 (s, 8H), 7.75 (t, 4H, *J* = 6.3 Hz), 8.18 (d, 4H, *J* = 7.5 Hz), 8.33 (s, 4H), 9.01 (d, 4H, *J* = 4.8 Hz). IR (KBr, cm⁻¹): 845 (s, PF₆). [(en)PdL]₂(PF₆)₄ and [(bpy)PdL]₂(PF₆)₄ were synthesized by the similar method.

Dioxane-Adsorption and -Desorption on Swellable Submicrospheres. The puckered submicrospheres were immersed in a mixture of water and dioxane (1 : 1) for 2 h, and were dried in a vacuum oven at room temperature to produce the filled submicrospheres. The filled submicrospheres were dried in a vacuum oven at 70 °C to obtain the puckered submicrospheres.

Results and Discussion

Preparation. The ionic palladium(II) complex was prepared by the reaction of (tmeda)Pd(PF₆)₂ with L. The ionic palladium(II) complex of L containing a hydrophobic long chain, [(tmeda)PdL]₂(PF₆)₄, gave white puckered submicrospheres in a 70% yield *via* evaporation of acetone at ambient temperature from a mixture of acetone and water depicted in Scheme 1. The product was collected by the filtration using a membrane (membrane filter, Advantec MFS Inc.). The puckered submicrospheres were characterized by elemental analysis, ¹H NMR, IR (ν(PF₆) = 844 cm⁻¹), contact angle, thermal analysis, and SEM. In order to measure the molecular weight of the palladium(II) complex, the product was dissolved in acetone (~ 10⁻⁴ M), and then the

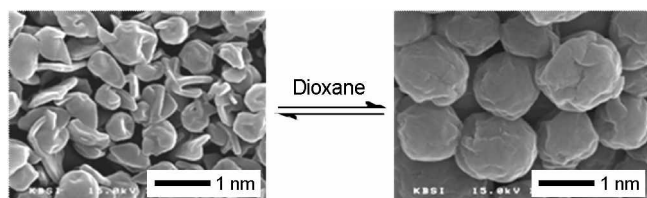
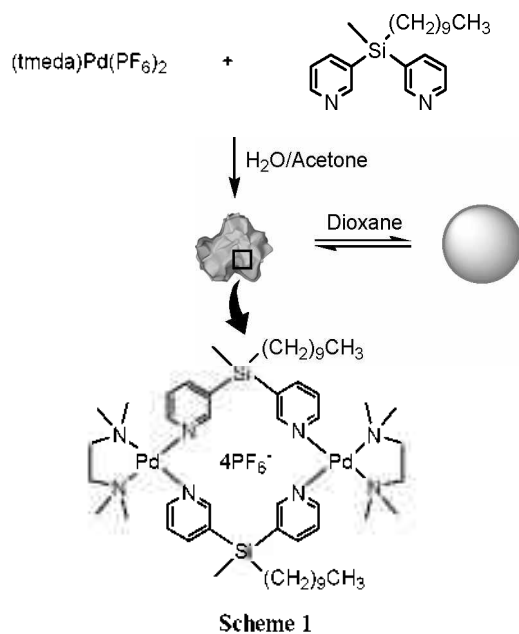


Figure 1. SEM images of the pucker and the filled submicrospheres consisting of $[(\text{tmeda})\text{PdL}]_2(\text{PF}_6)_4$.

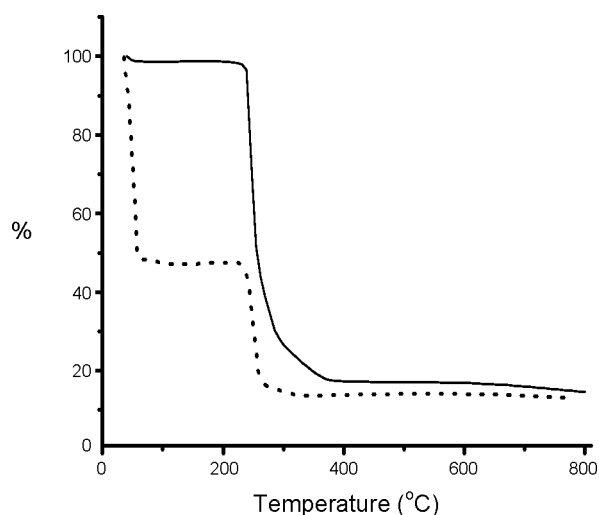


Figure 2. TGA data of $[(\text{tmeda})\text{PdL}]_2(\text{PF}_6)_4$. Solid line: pucker submicrospheres. Dashed line: swelled submicrospheres filled with dioxane molecules.

solution was mixed with 3-nitrobenzyl alcohol on an FAB probe tip (Supporting Information). The molecular weight was identified by the presence of the following ions at $m/z = 1562$ $[\text{M}-\text{PF}_6]^-$, 1417 $[\text{M}-\text{PF}_6-\text{HPF}_6]^-$, 1301 $[\text{M}-\text{PF}_6-(\text{HPF}_6)_2]^+$, and 1049 $[\text{M}-\text{PF}_6-(\text{HPF}_6)_3]^+$, indicating that the structure of the ionic palladium(II) complex is a cyclodimer, $[(\text{tmeda})\text{PdL}]_2$

$(\text{PF}_6)_4$. Furthermore, similar dimeric structures were elucidated by X-ray crystallography.^{25,30} The part around palladium(II) cation and PF_6 counteranions seems to be hydrophilic, and L moiety with a new long aliphatic chain seems to be hydrophobic. Of course, L itself doesn't form the submicrospherical morphology. Such an amphiphilic solubility may be a driving force for the formation of spherical morphology. Formation of the pucker submicrospheres may be ascribed to the presence of the long aliphatic hydrocarbon groups. That is, the hydrophobic long chain induces the formation of submicrospheres containing acetone molecules. The acetone-evaporation of the submicrospheres produces the pucker submicrospheres. The product is hardly soluble in water, but is soluble in a mixture of water and acetone.

Properties of Swellable Submicrospheres. The pucker submicrospheres were immersed in a mixture of water and dioxane for 2 h to afford the filled submicrospheres with diameters in the range of 500 ~ 800 nm. As the dioxane is pumped away, the submicrospheres are pucker but retained their structural integrity. The SEM image of the pucker submicrospheres was shown in Figure 1. They easily adsorbed and desorbed dioxane molecules in a mixture of water and dioxane. SEM images of the adsorbed submicrospheres are more spherical than the pucker desorbed submicrospheres, indicating that the submicrospheres are reversibly pucker and filled. Dioxane molecules are adsorbed into the spheres in only a mixture of water and dioxane. That is, the dioxane-adsorption was not observed in pure dioxane solvents, suggesting that water molecules play a key role in the adsorption-process. In order to quantify the information on the adsorbed dioxane molecules, the TGA curves of the pucker and the filled submicrospheres were measured (Figure 2). The TGA shows that 50 wt% dioxane molecules were contained inside the submicrospheres. The dioxane molecules were evaporated in the 70 ~ 100 °C temperature range as depicted in Figure 2. The thermogravimetric analysis (TGA) indicates that the skeletal structure is thermally stable up to 220 °C. The product drastically collapses around 220 ~ 300 °C. ^1H NMR spectrum of a simple mixture of D_2O and dioxane- d_8 was compared with the mixture solution after the immersion of the pucker submicrospheres. For the treatment-after solution, the dioxane signals significantly decreases (Supporting Information). Such a fact indicates that the pucker submicrospheres can be useful to membrane for specific organic solvent. This swellable submicrospheres may be applied to small molecular sensor, membrane, and delivery system.²⁶

Coligand and Cosolvent Effects on the Formation of Submicrospheres. All of the complexes produced spherical morphologies. In contrast to the swellable submicrospheres consisting of $[(\text{tmeda})\text{PdL}]_2(\text{PF}_6)_4$, $[(\text{en})\text{PdL}]_2(\text{PF}_6)_4$ yields smooth submicrospheres, and $[(\text{bpy})\text{PdL}]_2(\text{PF}_6)_4$ affords much bigger chestnutbur microspheres as shown in Figure 3. These results indicate that the formation of spheres is very sensitive to coligands. The coligands such as tmeda, en, and bpy are different in amphiphilicity and solubility. The more hydrophobic coligands make the morphology pucker even in solution, owing to the the presence of organic solvent during the formation of morphology. For $[(\text{bpy})\text{PdL}]_2(\text{PF}_6)_4$, high crystallinity of bpy coligand may attribute to form the chestnutbur morphology. When ethyl alcohol or

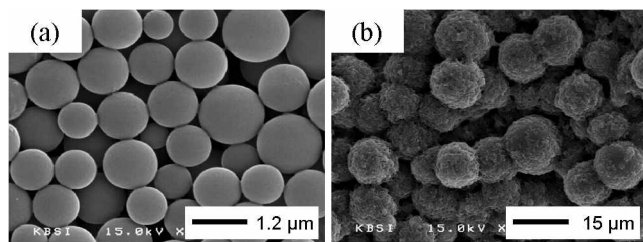


Figure 3. The morphology of $[(en)PdL]_2(PF_6)_4$ (a) and $[(bpy)PdL]_2(PF_6)_4$ (b).

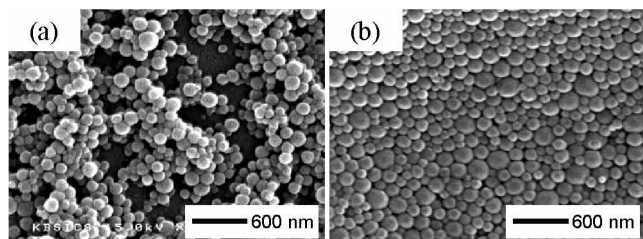


Figure 4. The submicrospheres of $[(tmeda)PdL]_2(PF_6)_4$ from a mixture of water and ethyl alcohol (a) and a mixture of water and isopropyl alcohol (b).

isopropyl alcohol instead of acetone as a cosolvent was used. $[(tmeda)PdL]_2(PF_6)_4$ produced smaller spheres with 100 nm ~ 150 nm diameters, even though the evaporation rate of alcohol is slower than acetone (Figure 4). The hydroxyl group plays a significant role in the formation. The hydrogen bonding between the product and alcohol seems to retard the evaporation of solvent compared to acetone. Isopropyl alcohol produces the more compact submicrospheres, indicating that the evaporation rate of isopropyl alcohol is slower than that of ethyl alcohol.

In conclusion, the assembly of ionic palladium(II) complexes with a new long aliphatic chain in a mixture of water and organic solvent was proved to be an effective strategy for the preparation of swellable submicrospheres without addition of any template. Furthermore, the behavior of this product is very sensitive to coligand and cosolvent effects. Reversible interconversion between dioxane-adsorption and dioxane-desorption will contribute to the development of more detailed micro-based functional materials such as sensing materials, membrane, surface modifiers, and catalysts.

Acknowledgments. This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

Supporting Information. IR spectra of ligand (L), 1H NMR, contact angle, mass, and IR spectra of $[(tmeda)PdL]_2(PF_6)_4$. The

information is available on request from the correspondence author.

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