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Formation and Related-Behavior of Micro-bowl Morphology Consisting of Ionic Palladium(II) Complexes

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Reaction of $[(bpy)Pd](PF_6)_2$ (bpy = 2,2'-bipyridine) with racemic bis(isonicotinoyl)-1,1'-bi-2-naphtholate (L) in acetone, and followed by addition of chloroform and solvent evaporation allows to form amorphous micro-bowl morphology consisting of $[(bpy)PdL]_2(PF_6)_4$ without any template or additive. In contrast, the reaction and recrystallization in acetone for 1 week produce parallel-piped single crystals consisting of $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$. The formations of micro-bowl and parallel-piped single crystal morphologies appear to be primarily associated with the kinetic and thermodynamic control, respectively. The formation of micro-bowls may be attributed to eruption of organic solvents. Cosolvent effects and chemical properties on the formation of micro-bowl morphology have been observed.

Key Words: Amphiphilic properties, Ionic palladium(II) complex, Micro-bowl morphology, SEM image, Solvent eruption

Introduction

Research on the manipulation of unique micro morphologies remains central to the achievement of task-specific micro-materials such as catalysts, electronic devices, drug-delivery systems, ceramics, pigments, and cosmetics.[1-8] Prediction of such morphological properties on the basis of molecular structure is a current hot issue.[9-16] Thus, in order to grow unusual non-spherical morphology, steric effects, surface tension, capillary effects, electric and magnetic forces, permanent dipoles, van der Waals interaction, hydrophilic interactions, surfactant/precursor ratio, covalent bond, and shape anisotropy have been applied as significant driving forces.[17-23] In particular, microsphere with hollow interiors play important roles in micro-encapsulation such as drug delivery system, cosmetics, inks, pigments, and removal of pollutants. Molecular assembly based on metal-ligand coordination has been proven to be an effective strategy for the facile preparation of micro mono-disperse morphology.[14,24,25] Even though a few follow spheres have already been reported,[26] the morphogenesis of micro-bowl shape remains rare.

In this context, this paper reports a straightforward method and outgrowth results for the morphogenesis of micro-bowl consisting of ionic palladium(II) complexes without addition of any additives. Micro-bowls were formed by the reaction of $(bpy)Pd(PF_6)_2$ (bpy: 2,2'-bipyridine) with racemic bis(isonicotinoyl)-1,1'-bi-2-naphtholate (L). The complex in solution was slowly changed to a thermodynamically stable hydrolysis product.

Experimental

Materials and measurements. All chemicals including potassium tetrachloropalladate(II) and 2,2'-bipyridine (bpy) were purchased from Aldrich Chemicals, and used without further purification. $(bpy)PdCl_2$[27] and bis(isonicotinoyl)-1,1'-bi-2-naphtholate (L)[28] were synthesized according to each reference. Elemental microanalyses (C, H, N) were performed on samples by the Pusan Center at KBSI using a Vario-EL III. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz, and the chemical shifts were relative to the internal Me_4Si. ^{31}P NMR (121.00 MHz) spectra were recorded on a Varian Unity Plus 600 relative to the internal H_3PO_4. Infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with samples prepared as KBr pellets. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600. Mass spectrometric analysis was performed in methanol by KMS-700 Mstation Mass Spectrometer (Jeol, Japan) using a MS-MP9020D data system. Scanning electron microscope images were obtained on a JEM 2011.

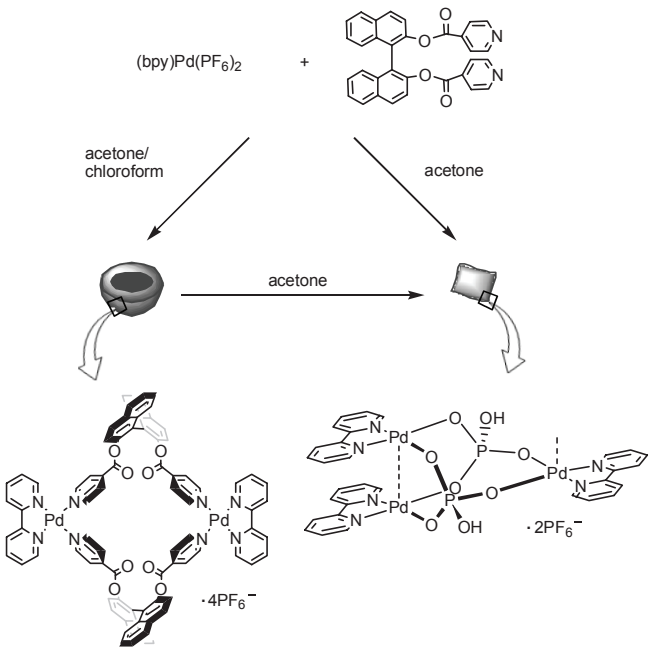
Micro-bowl, $[(bpy)PdL]_2(PF_6)_4$. $(bpy)PdCl_2$ (16.6 mg, 0.05 mmol) was suspended in acetone (5 mL) and stirred for 2 h at room temperature with $AgPF_6$ (25.2 mg, 0.1 mmol). After removal of AgCl by filtration, L (24.8 mg, 0.05 mmol) in acetone (5 mL) was slowly added to the filtrate. The mixture was refluxed for 2 h. Chloroform (3 mL) was poured into the mixture and then the mixed solution was slowly evaporated for 2 days to give white precipitate of $[(bpy)Pd(L)]_2(PF_6)_4$ in an 80% yield (83.9 mg). Anal. Calc. for $C_{84}H_{56}N_8O_8P_4Pd_2$: C, 48.09; H, 2.69; N, 5.34%. Found: C, 47.50; H, 2.60; N, 5.21%. IR (KBr, cm^{-1}) 1751 (s, ν(CO)), 1450, 1277, 1099, 843 (br, ν(PF_6)), 764, 557 (ν(PF_6)). ^{1}H NMR (Me_2SO-d_6, $SiMe_4$, δ) 8.66 (d, J = 3.9 Hz, 8H), 8.62 (overlapped with the adjacent peak of 8.66 ppm, 4H), 8.47 (d, J = 6.0 Hz, 4H), 8.30 (t, J = 7.2 Hz, 4H), 8.18 (d, J = 9.3 Hz, 4H), 8.08 (d, J = 8.4 Hz, 4H), 7.83 (t, J = 10.5 Hz, 4H), 7.71 (d, J = 7.8 Hz, 4H), 7.56 (t, J = 6.9 Hz, 4H), 7.43 (t, J = 7.2 Hz, 4H), 7.40 (d, J = 6.0 Hz, 8H), 7.19 (d, J = 7.5 Hz, 4H). FAB Mass m/z 897 $[M\text{-}2PF_6^-]^{2+}$, 718.5 $[M\text{-}L\text{-}PF_6^-]^{2+}$, 710 $[M\text{-}bpy\text{-}PF_6^-]^{2+}$, 598 $[M\text{-}2PF_6^-]^{3+}$.

Single crystal, $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$. The reaction

Table 1. Crystal data and structure refinement for $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2{\cdot}CH_3OH$.

Empirical formula	$C_{31}H_{30}N_6O_9F_{12}P_4Pd_3$
Formula weight	1301.69
Crystal system	Monoclinic
Space group	*C*2/m
a, Å	28.478(7)
b, Å	13.054(4)
c, Å	12.841(3)
β, deg	109.933(1)
V, Å^3	4487.4(2)
Z	4
d_{cal}, gcm^{-3}	1.925
μ, mm^{-1}	1.437
Completeness to theta = 26.00°	100.00%
Data / restraints / parameters	8973/2/327
Goodness-of-fit on F^2	1.088
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0486$, $wR_2 = 0.1420$
R indices (all data)	$R_1 = 0.0520$, $wR_2 = 0.1473$

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^2]^{1/2}$



Scheme 1. Synthetic procedure.

was carried out by the similar method, and then was left for 1 week without addition of chloroform. After one week, pale yellow crystals suitable for X-ray crystallography were obtained in a 78% yield (49.5 mg). Anal. Calc. for $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2{\cdot}CH_3OH$, $C_{31}H_{30}N_6O_9F_{12}P_4Pd_3$: C, 28.60; H, 2.32; N, 6.46%. Found: C, 28.50; H, 2.47; N, 6.40%. IR (KBr, cm^{-1}) 1603 (s, ν(CO)), 1171 (s, ν(HPO_4)), 1448, 1007, 837 (br, ν(PF_6)), 719, 768, 561 (ν(PF_6)). ^{1}H NMR (Me_2SO-d_6, $SiMe_4$, δ) 8.60 (d, J = 4.2 Hz, 6H), 8.51 (d, J = 4.8 Hz, 6H), 8.44 (br, 6H), 7.88 (t, J = 7.2 Hz, 6H).

Crystal structure determination of $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2{\cdot}CH_3OH$. X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a CCD detector at ambient temperature. Thirty six frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the empirical SADABS method. The structures were solved using the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).[29] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1. Hydroxyl group in the phosphate was disordered (occupancy (O(4) : O(4)') = 46% : 54%). Since the large positive (2.00 e Å^{-3}) and negative (−1.61 e Å^{-3}) difference Fourier peaks are located at short distances from Pd(2) (0.66 Å) and Pd(1) (0.82 Å), respectively, these peaks can be attributed to ghosts of the heavy Pd atoms. The methanol solvate molecules came from the synthetic procedure of (bpy)$PdCl_2$ in methanol.[27] Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (CCDC-761371). The data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis and properties. Reaction of (bpy)$Pd(PF_6)_2$ with L in acetone, and followed by addition of chloroform (3 mL) into the acetone (10 mL) solution of $[(bpy)PdL]_2(PF_6)_4$, and then slow evaporation of solvents gave white product of micro-bowls as depicted in Scheme 1. The micro-bowl product was collected by the centrifuge (Advantec MFS Inc.) for further characterization. The product is marginally insoluble in water and common organic solvents such as acetone, chloroform, dichloromethane, and benzene, but is soluble in a mixture of water and acetone, reflecting that the complex is amphiphilic properties. In this study, the product was dissolved in a mixture of water and acetone, which the solution was mixed with 3-nitrobenzyl alcohol on a FAB probe tip in order to measure the molecular weight of the Pd(II) complex. The mass data indicated that the product consists of a cyclodimeric structure (m/z = 897, $[M\text{-}2PF_6^-]^{2+}$; m/z = 748, $[M\text{-bpy-}HPF_6\text{-}2PF_6^-]^{2+}$; Supporting Information). The micro-bowl product was characterized by ^{1}H NMR, IR (ν(CO) = 1751 cm^{-1}; ν(PF_6) = 843 cm^{-1}), and SEM image along with satisfactory chemical analysis. SEM image shows that the micro-bowls have diameters in the range of 300 nm −1 μm as shown in Figure 1. Evaporation of chloroform seems to give the micro-bowls. The quantity of chloroform (acetone : $CHCl_3$ = 10 : 3) is a significant factor for the formation of the micro-bowl morphology. Moreover, in a mixture of acetone and diethyl ether, such a morphology was not formed, and instead submicrospheres were formed, indicating that the solvent plays an important role in the formation of the morphology. In contrast, the reaction of (bpy)$Pd(PF_6)_2$ with L in acetone, and then left for

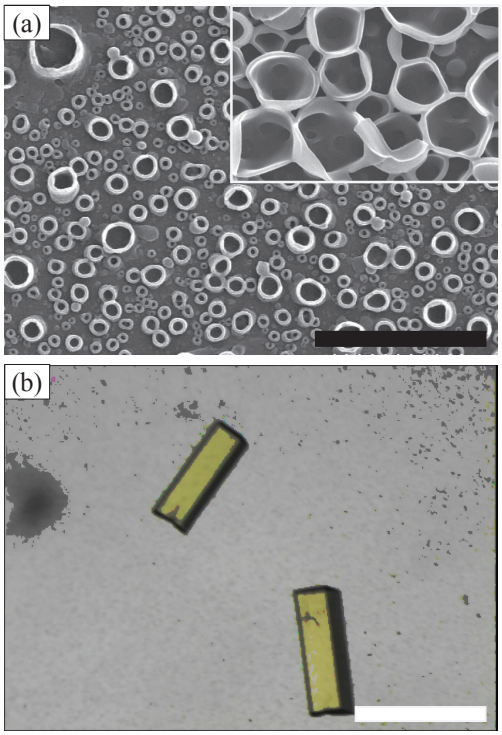


Figure 1. SEM images of micro-bowl (a) and optical microscopic image of crystals (b). black bar = 3 μm, white bar = 0.1 mm.

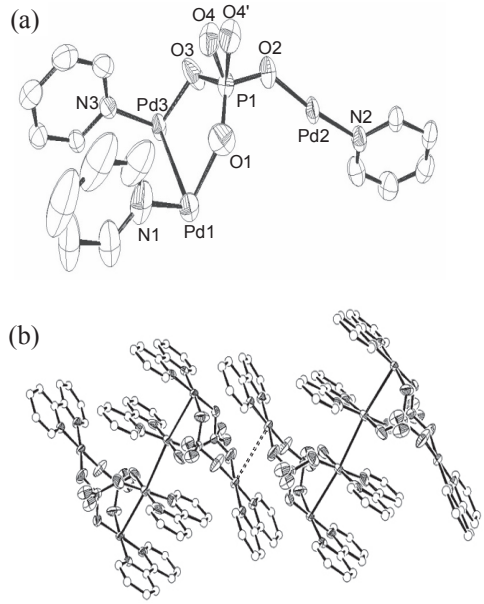


Figure 2. Asymmetric unit (a) and packing diagram (b) of crystal. The O4 was disordered. Hydrogen atoms, anions, and solvated methanol were omitted for clarity.

1 week to obtain thin yellow single crystals consisting of hydrolysis products, $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$ which will be discussed by X-ray crystallography in detail. HPO_4^{2-} seems to come from the hydrolysis of PF_6^-. PF_6^- has been known to be slowly decomposed with release of HF in aqueous solution.[30] Such a fact indicates that the dimeric species, $[(bpy)PdL]_2(PF_6)_4$, is not stable for a long time in solution.

Table 2. Bond lengths [Å] and angles [°] for $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$.

Pd(1)-N(1)	1.975(3)	N(1)-Pd(1)-N(1)$^{\#1}$	82.0(2)
Pd(2)-N(2)	1.975(3)	O(1)-Pd(1)-O(1)$^{\#1}$	90.3(3)
Pd(3)-N(3)	1.981(5)	N(2)-Pd(2)-N(2)$^{\#1}$	81.9(2)
Pd(1)-O(1)	2.002(4)	O(2)-Pd(2)-O(2)$^{\#1}$	95.8(2)
Pd(2)-O(2)	2.006(4)	N(3)-Pd(3)-N(3)$^{\#1}$	81.5(4)
Pd(3)-O(3)	2.015(4)	O(3)-Pd(3)-O(3)$^{\#1}$	88.8(2)
P(1)-O(1)	1.478(3)	O(1)-P(1)-O(2)	112.7(3)
P(1)-O(2)	1.463(3)	O(2)-P(1)-O(3)	115.3(2)
P(1)-O(3)	1.493(3)	O(1)-P(1)-O(3)	115.2(2)
Pd(1)-Pd(3)	3.006(5)		
Pd(3)-Pd(3)$^{\#2}$	3.070(7)		
Pd(2)···Pd(2)$^{\#3}$	3.649(8)		

Symmetry transformations used to generate equivalent atoms: #1 x, -y,z #2 -x+1,-y,-z+1 #3 1-x,y,-z.

X-ray crystal structure of $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$. X-ray characterization on a single crystal has provided the structure of $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$, and its relevant bond lengths and angles are listed in Table 2. The X-ray crystal structure shows a centrosymmetric dimeric species *via* Pd(II)···Pd(II) interactions as depicted in Figure 2. HPO_4^{2-} connects three Pd(II) cations (Pd-O = 2.002(4) − 2.015(4) Å) in a μ_3-fashion to form $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$. The hexafluorophosphate anion acts as a counteranion rather than a ligand (the shortest Pd(II)···F = 5.560(9) Å). Thus, the geometry around the Pd(II) ion approximates a typical square planar arrangement (N(1)-Pd-N(1)' = 82.0 (2)°, N(1)-Pd-O(1) = 93.8 (2)°, O(1)-Pd-O(1)' = 90.3 (3)°). Three kinds of Pd(II)···Pd(II) interactions of intramonomeric Pd···Pd (3.006(5) Å), intradimeric Pd(II)···Pd(II) (3.070(7) Å), and interdimeric Pd(II)···Pd(II) (3.649(8) Å)[31] exist in the solid state, and thus to form 1-D coordination polymer. The polymeric species may be stabilized *via* an intramolecular face-to-face π-π stacking (N(1)···N(3) = 3.497(5) Å, dihedral angle = 5.8(3)°, center to center = 3.651(1) Å).

Formation and properties of amorphous micro-bowls and parallel-piped single crystals. Formation of the micro-bowls may be ascribed to prompt eruption of solvated organic molecules inside the microspheres. The micro-bowls may be applied to small molecular sensor, membrane, and delivery system. In specific solvent system, chloroform can be affect to formation of micro-bowl. That is, the bowl-morphology seems to have the best shape in ratio of specific organic solvent (chloroform/acetone = 3:10) (Supporting Information). The addition of diethyl ether as a co-solvent instead of chloroform produced the submicrospheres (Supporting Information). These results indicate that the formation of micro-bowls is very sensitive to both the kind and the ratio of solvents. The chemical composition of the submicrosphere was consistent with that of the micro-bowl morphology. Attempt to fill submicrospheres consisting of $[(tmeda)Pd(p\text{-}HM)]_2(ClO_4)_4$[32] into the micro-bowl was accomplished, but was not successful presumably owing to the same surface properties of inside and outside of the micro-bowls (Supporting Information).

The cause of the formation of the unique micro-bowl morphology is not clear at this stage, but most likely is a function of

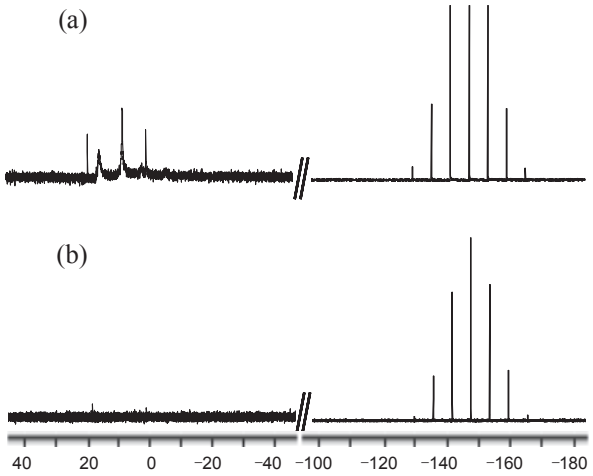


Figure 3. ^{31}P NMR (121 MHz) spectra of crystals (a) and micro-bowls (b) in Me_2SO-d_6.

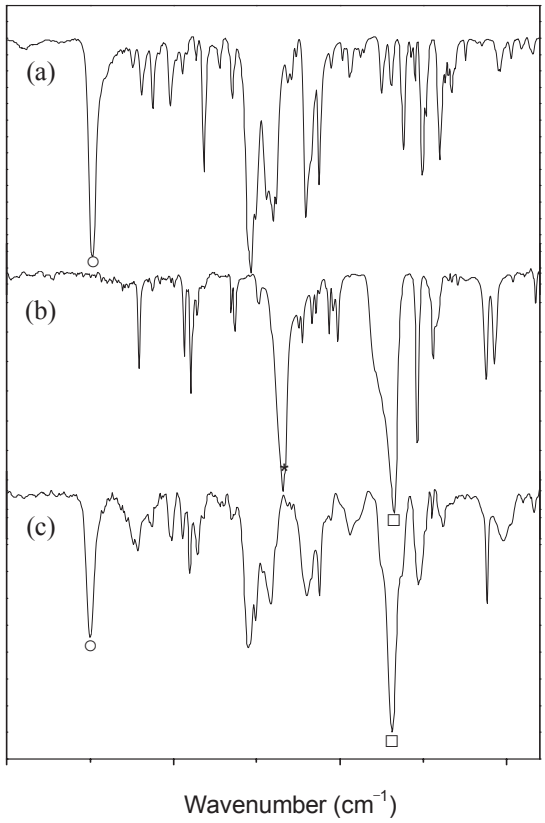


Figure 4. IR spectra of L (a), crystals (b), and micro-bowls (c). Circles, squares, and asterisks indicate the C=O, PF_6^-, and HPO_4^{2-}, respectively.

eruption of organic solvents. That is, the first stage swell the (sub)microspheres with chloroform, and the second stage evaporates chloroform by vacuum.[26] Swelling *via* solvent is a key factor for the formation of micro-bowl. Thus, the plausible growth mechanism can be explained as the follows: in the first stage, the submicrospheres form, after which, in the more dilute second stage, the eruption of organic solvents. Distinct differences in chemical composition (EDX), mass, and homogeneity (TEM) between the inside and the outside part were not observed, indicating that the inside and the outside have the same chemical structure. The TGA curve (Supporting Information) indicates that the skeletal micro-bowl was stable up to 250 ^{o}C, but evaporation in the range of 60 - 100 ^{o}C corresponded to the evaporation of chloroform solvent molecules (2 moles) inside the microsphere (9.4 wt %).

Solution-behavior of single crystalline product was characterized by ^{31}P NMR and ^{1}H NMR. The ^{31}P NMR shows the presence of both HPO_4^{2-} and PF_6^- in contrast to only PF_6^- peaks of the micro-bowl (Figure 3). The peaks of HPO_4^{2-} are 18.51, 14.95, 7.72, 0.34 ppm owing to the presence of 4 possible phosphate peaks, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4 in aqueous solution. Seven peaks around -150 ppm were assigned to ^{31}P signals of PF_6^-. IR frequency at 1171 cm^{-1} was assigned to $\nu(HPO_4^{2-})$ (Figure 4).

Conclusion

In conclusion, the assembly of ionic palladium(II) complexes containing racemic ligand in a mixture of acetone and chloroform was proved to be an effective strategy for the formation of micro-bowls without addition of any template. Furthermore, the morphology of this product is very sensitive to solvent and cosolvent effects. The structural modification of unusual micro-bowl morphology will contribute to the development of more detailed micro-based functional materials such as sensing materials, membrane, surface modifiers, and catalysts. Such a kind of complexes, productive of a diverse class of micromaterials, promises better materials models including a reaction micro-vessel, catalyst, drug delivery system in the future.

Supporting Information. SEM images of microspheres produced in a mixture of acetone/dichloromethane and acetone/ether solution. TGA data of $[(bpy)Pd(L)]_2(PF_6)_4$. FAB-Mass data of $[(bpy)Pd(L)]_2(PF_6)_4$. SEM images of attempt to fill submicrospheres into micro-bowls. SEM images of the micro-bowl produced in a mixture of chloroform/acetone solution. ^{1}H NMR spectra of ligand (L), $[(bpy)_3Pd_3(\mu_3\text{-}HPO_4)_2](PF_6)_2$, and $[(bpy)Pd(L)]_2(PF_6)_4$ in Me_2SO-d_6. The informations are available on request from the correspondence author.

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