First direct-formation and properties of microspherical superstructure. Morphology of diamineplatinum(II) complexes with isonicotinate†

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Uniform microspheres (30 μm) of [Pt(en)(iso)(iso·HPF_6)] (en = ethylenediamine; iso = isonicotinate) has been formed without intentional addition of any template, that is, a genuine self-assembly, and their structure, physicochemical properties, and hydrogenation-catalytic activity have been characterized.

The ability to modulate uniform superstructure/morphology by means of chemical triggers is of central importance in the recent development of advanced functional materials.[1–5] Unique morphologies from molecular building blocks promise to provide size- and shape-dependent materials with task-specific properties such as photo-electronic devices, pigments, ion exchangers, dessicants, molecular recognizers, drug delivery systems, biomimetics and catalysts.[1–9] In particular, facile methods for the formation of nano-/micro-spherical morphology based on surface tension, capillary effects, electric and magnetic forces, and hydrophilic interactions have been highly desired.[1,10–14] Various morphologies of metal chalcogenides have been widely produced, but the systematic morphogenesis of metal complexes remains unexplored. In this communication, we present the first direct formation and related properties of microspherical superstructures *via* the reaction of [PtX_2(N–N)] (X^- = PF_6^-, ClO_4^-, $CF_3SO_3^-$, NO_3^-, BF_4^-; N–N = ethylenediamine, *N*,*N*-dimethylethylenediamine) with triethanolaminetriisonicotinate (L) in water without intentional addition of any additive. The microspherical superstructue can be rapidly constructed *via* a facile method. To date, diamineplatinum(II) chemistry has been applied to various fields such as the isomerism of ambidentate ligands, the synthesis of antitumor (pro)drugs, the building block of square grids, and the preparation of luminescent materials *via* special interaction, and catalysts.[15–18]

Reaction of [Pt(PF_6)$_2$(en)] (en = ethylenediamine) with L in water, and then evaporation of solvent gave a uniform microspherical morphology consisting of [Pt(en)(iso)(iso·HPF_6)] (iso = isonicotinate obtained by the hydrolysis reaction of L)‡ as shown in Scheme 1. The microspheres were characterized by elemental analysis, ^{1}H and ^{13}C NMR, IR, thermal analysis, contact angle, SEM, and X-ray powder diffraction. Elemental analysis and IR (ν(PF_6) = 839 cm^{-1}) indicate that the product is an adduct of HPF_6. Two strong stretching bands at 1709 and 1601 cm^{-1} indicate the coexistence of –COOH and –COO$^-$ in the product, suggesting that a carboxylate moiety interacts with the added HPF_6. ^{1}H and ^{13}C NMR spectra in D_2O show that the ratio of iso to en is 2 (ESI†). The side-product triethanolamine·HPF_6 was isolated and characterized. The microspheres dissolve slowly in hot water but are insoluble in common organic solvents. The spherical morphology of the as-synthesized sample was revealed by SEM (Fig. 1). The diameter of the mature spheres is about 30 μm. The microspheres consist of about 100 nm needle-like crystals. X-Ray powder diffraction peaks indicate that the microspheres are aggregates of small crystals (ESI†). The most striking feature is that the spherical morphology is rapidly formed. The microspheres slowly dissolve in an aqueous alkaline solution of 0.05 M $NaHCO_3$. When the microspheres were left in the solution for 2 days, the shells of the microspheres were isolated from the cores, as shown in Fig. 2. Such a result indicates that the core/shell interface is mechanically unstable. Thus, the core is easily removed from the 7 μm thick shell. The thickness is ascertained from the difference in size between the sphere in Fig. 1(c) and the sphere in Fig. 1(d). The *N*,*N*-dimethylethylenediamine (dmeda) analogue was prepared in order to investigate the coligand effects. The dmeda analogue produced a similar spherical morphology, but slightly bigger (40–50 μm) spheres. For the dmeda sphere, the unit nanocrystal is a clear parallelepiped crystal (ESI†). The same reactions of [Pt(en)X_2] (X^- = ClO_4^-, $CF_3SO_3^-$, $NO_3^-$and BF_4^-) with L were attempted to scrutinize counteranion effects.[19,20] For the various anion analogues, aggregates of small crystals were formed, but their morphologies were not a uniform spherical shape. Furthermore, in order to abstract the HPF_6 from [Pt(en)(iso)(iso·HPF_6)], addition of extra triethanolamine in the reaction expectedly gives single crystals of [Pt(en)(iso)$_2$] instead of the spherical morphology. This fact indicates that the added HPF_6 plays an important role in the formation of the microspherical morphology.

The multicrystalline aggregates form spontaneously if $\Delta G < 0$ (free energy of the formation of spherical morphology). The present molecule owes its properties to the combination of a polar carboxylate group and a less polar tail moiety. The solubility of the microspheres provides significant information on the structural properties. The microspheres are most soluble in a mixture of water and acetone (1 : 1) rather than pure water or pure acetone, indicating that the compound has both hydrophilic and hydrophobic moieties. The molecules can crystallize in anisotropic unit nanocrystals. In an aqueous medium, a large number of nanocrystals consisting of the soap-like molecules congregate in

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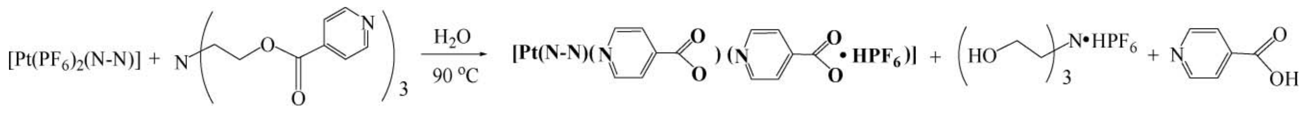
† Electronic supplementary information (ESI) available: ^{1}H, ^{13}C NMR, IR, thermal analysis, XRD of [Pt(en)(iso)$_2$](HPF_6). SEM images of analogues, water contact angle, structure of [Pt(en)(CH_3iso)$_2$](PF_6)$_2$, GC chromatogram and ^{1}H NMR of hydrogenated product. See DOI: 10.1039/b613044e



Scheme 1 Synthetic route towards microspherical superstructures.

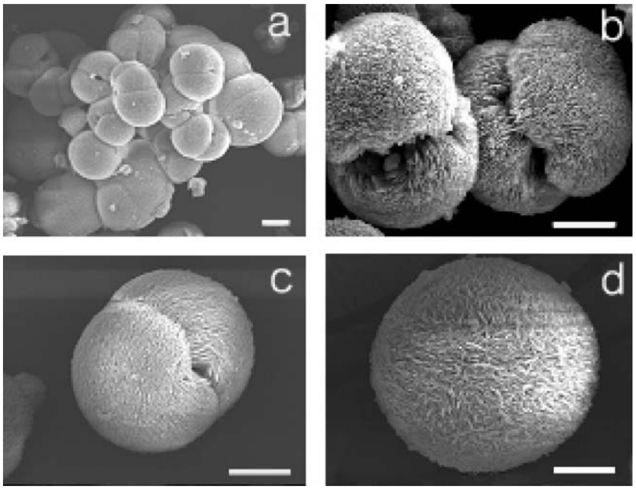


Fig. 1 SEM image of spherical superstructures in the bulk of [Pt(en)(iso)(iso·HPF_6)] (a), and high magnification SEM images showing the growth procedure of microspheres (b, c, d). Bar, 10 μm.

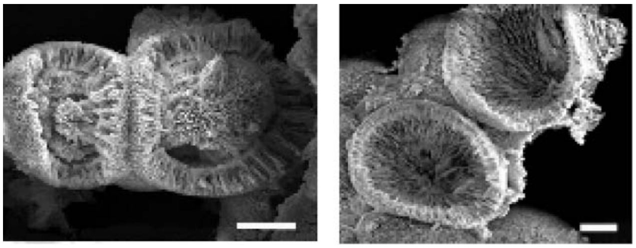


Fig. 2 SEM images of the core/shell assembly of [Pt(en)(iso)(iso·HPF_6)] (left). The core was removed from the shell (right). Bar, 10 μm.

a micellar type of spherical supercrystals. The water contact angle (52–57°) of the monolayer of the microspheres indicates that the microspherical surface is hydrophilic. The contact angle of the microspherical monolayer is much smaller than that of a polyethylene film (105–108°) (ESI†). A combination of micelle and anisotropic interfacial tension may be a driving force for the formation of the spherical superstructures. Fig. 1(b)–(d) show that the microspheres form according to the fractal model through dumbbell shape aggregates (ESI†).[12] The dipolar properties of [Pt(en)(iso)(iso·HPF_6)] support the formation-mechanism of the spheres *via* the fractal model. For the present reaction, the temperature, needless to say, is another important factor for the formation of the microspheres. The morphology is obtained in high yield only above 90 °C because the reaction is accompanied by the hydrolysis of ligand. The same reaction in methanol instead of water gives crystals of [Pt(en)(CH_3iso)$_2$](PF_6)$_2$ (CH_3iso = methyl isonicotinate) (for crystal structure see ESI†) *via* methanol transesterification of L. Use of an aqueous solution plays an important role in the formation of the spherical morphology. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) show that the compound is thermally stable up to 283 °C. According to the TGA curve, the ligand moiety of (iso)(iso·HPF_6) seems to collapse around 300 °C, and the en is removed around 600 °C. The explainable TGA and DSC curves support that the microspheres are composed of pure materials (ESI†).

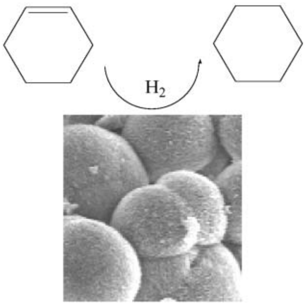


Fig. 3 Hydrogenation of cyclohexene.

In order to test the catalytic effects of the microspherical morphology, a preliminary hydrogenation was achieved depicted in Fig. 3: when hydrogen gas (3.5 bar) is bubbled into a methanol solution (20 mL) of cyclohexene (2 mL) containing 55 mg of the microspheres as a catalyst for 2 h, the substrate was completely hydrogenated (turnover number = 217). When 40 mg of the catalyst was used, the yield was about 70%. Thus, the yields of the hydrogenation (including other attempts) are proportional to the quantity of the micro-superstructures (ESI†). Hydrogenation was also attempted in ethanol or acetone, but the yield is the highest in methanol. After the hydrogenation reaction, the spherical morphology of most catalysts remains without a drastic collapse (ESI†).

In conclusion, (1) the present case is a rare spherical superstructure of fully characterized metal complexes. (2) The uniform microspheres are formed in water without intentional addition of any template, that is, a genuine self-assembly. (3) The microspheres could be rapidly formed *via* direct facile reaction. (4) The spherical superstructure is a good catalyst for hydrogenation. (5) Both amphiphilic solubility and the hydrophilic surface may be useful to a drug delivery system. Thus, further experiments on the superstructures with a hydrophilic surface will provide more useful information on the enormous potentials such as anticancer reagents, adsorber/desorbers, and surface-reformers.

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Notes and references

‡ Microspherical morphology of [Pt(en)(iso)(iso·HPF_6)]: An aqueous solution (10 mL) of [Pt(PF_6)$_2$(en)] (163 mg, 0.3 mmol) was slowly diffused into an aqueous suspension (20 mL) of triethanolaminetriisonicotinate (139 mg, 0.3 mmol), and then stirred at 90 °C for 2 h. Finally the reaction solution was condensed to 3 mL, resulting in white homogeneous microspheres in 70% yield; mp 283 °C (decomp.). Anal. Calc. for

$C_{14}H_{17}N_4O_4F_6PPt_3$: C, 26.06; H, 2.66; N, 8.68. Found: C, 26.40; H, 2.70; N, 8.58%. IR (KBr, cm^{-1}): ν(COOH), 1709(s); ν(COO), 1601(s) ν(PF_6), 839 (s). ^{1}H NMR (300 MHz, D_2O, Me_4Si): δ 8.92 (d, 4H), 7.76 (d, 4H), 5.94 (s, NH_2), 2.76 (s, CH_2). ^{13}C NMR (125.76 MHz, D_2O, Me_4Si): δ 168.8, 152.4, 146.0, 126.3, 47.9.

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