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Supramolecular Assemblies with Symmetrical Octahedral Structures – Synthesis, Characterization, and Electrochemical Properties

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Functional nanosized cage complexes with an octahedral framework have been synthesized by the facile self-assembly reactions of six 90° Pd^{II}-containing compounds {[Pd(dppf)-(OTf)₂] or [Pd(PPh₃)(OTf)₂], dppf = 1,1'-bis(diphenylphosphanyl)ferrocene, OTf = trifluoromethylsulfonate} and four 120° functional tritopic ligands [2,4,6-tri(4-pyridyl)-1,3,5-triazine] in acetone. Diffusion-ordered NMR spectroscopy (DOSY) and AFM images clarify the formation of 3–4 nm

Introduction

Multifunctional polymers^[1] and dendrimers^[2] have received wide research interest, because they can potentially be employed in the design of functionalized nanomaterials and devices. Traditionally, these functional materials are synthesized by using covalent synthetic protocols, which often suffer from rather time-consuming procedures, very low yields and largely uncertain final structures. Recently, a new coordination-driven self-assembly method has been proposed as a powerful alternative technique for the efficient synthesis of such multifunctional polyhedral molecules, because it allows for the incorporation of multiple functional centres of various geometries and properties. To obtain a deeper understanding of the nature of such coordination-driven self-assembly processes, a great deal of effort has been made to investigate artificial functional supramolecular systems. For example, Stang et al.^[3] have reported an interesting route to snowflake-shaped metallodendrimers with hexagonal cavities as their cores. Fujita^[4] and coworkers have prepared saccharide-coated molecular spheres that form aggregates after interactions with pro-

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nanoparticles. These highly symmetrical cage complexes are discrete, face-directed, functional nanoparticles with symmetrical octahedral structures. The self-assembled functional cage complexes exhibit interesting electrochemical activities, and thus will potentially be useful in the catalysis of redox reactions, the encapsulation of sizeable guest molecules and the control of organic synthetic reactions.

teins. We have presented an instantaneous synthetic route for the preparation of thiophene-coated functional nanospheres that show interesting electrochemical properties.^[5] These initial studies have demonstrated that the introduction of functional groups to individual building blocks results in new multifunctionality and controllable structures on the basis of the original topology of the assembling polyhedral molecules. These thermodynamically and kinetically stable transition metal complexes can exhibit thermo-, chemo- and mechanoresponses, as well as light-emitting properties.^[6–8]

In particular, cavity-cored polyhedral molecules have received considerable attention because of their elaborate structures and potential applications in molecular recognition and sensors. For example, supramolecular octahedral nanocages have unique hollow structures that allow them to play essential roles in the fields of encapsulation of sizeable guests,^[9] control of organic synthetic reactions^[10] and catalysis of redox reactions.^[11] A highly symmetric octahedral M₆L₄ structure can be synthesized when six 90° ditopic metal units (M) combine with four 120° planar tritopic ligand units (L).^[12] Generally, these octahedral molecules have been prepared in water, and the resulting octahedra are water soluble mainly because of the properties of the corresponding cation (NO_3^{-}) . These octahedral molecules can have a large hydrophobic cavity that can encapsulate sizeable guest molecules in water. However, highly symmetric octahedral complexes that have a nanoscopic hollow cavity have been scarcely reported in organic phase systems. Thus, stimulated by the power and versatility of coordina-



tion-driven self-assembly, we present a new type of symmetric octahedral molecule that is soluble in common organic solvents instead of an aqueous solvent system. Moreover, functional moieties can be attached at different positions around the periphery of the octahedral structures. Thus, the supramolecular self-assembly allows us to precisely control the shape and size of the resulting molecules as well as the distribution and total number of incorporated functional moieties.^[13]

Here, we report the preparation of functionalized M_6L_4 cage complexes through the facile self-assembly reactions of six 90° ditopic Pd^{II}-containing [Pd(dppf)(OTf)₂] [1, dppf = 1,1'-bis(diphenylphosphanyl)ferrocene, OTf = trifluoromethylsulfonate] or [Pd(PPh₃)(OTf)₂] (2) subunits and four 120° tritopic 2,4,6-tri(4-pyridyl)-1,3,5-triazine (3) ligand subunits in acetone solution (Scheme 1). The cage structure has a very large conjugated range owing to the triazine groups linked with three pyridine rings in every ligand subunit. Two functional Pd^{II} building blocks (1 and 2) were considered that include bis(diphenylphosphanyl)ferrocene or bis(triphenylphosphanyl) moieties, respectively, at the vertex of the 90° Pd^{II} metal subunit. The generated complexes (4 and 5) were insoluble in water, but soluble in organic solvents, mainly owing to the presence of six cationic Pd^{II} centres (containing trifluoromethylsulfonate, OTf⁻). The 90° ferrocenyl-substituted precursor 1 [Pd(dppf)-(OTf)₂] and the triphenylphosphanyl-substituted precursor 2 $[Pd(PPh_3)(OTf)_2]$ can be easily prepared by ion exchange reactions between [Pd(dppf)Cl₂] or [Pd(PPh₃)Cl₂] and Ag-OTf. [Pd(dppf)Cl₂] and [Pd(PPh₃)Cl₂] are two common Suzuki and Heck reaction palladium catalysts and can be easily obtained. Thus, by suspending the tritopic ligand 3 in an acetone solution of the precursor 1 or 2 in the ratio of 2:3, we obtained the assembled M_6L_4 complex 4 or 5. Although the ferrocenyl-substituted cage complex 4 is remarkably soluble in organic solvents such as acetone, acetonitrile, nitromethane, dimethyl sulfoxide (DMSO), and so on,



Scheme 1. Self-assembly reactions to prepare multifunctional octahedral complexes $M_6L_4\,4$ and 5 with six appended functional moleties.

the triphenylphosphanyl-substituted complex **5** is soluble only in more polar solvents such as acetone and DMSO. The synthetic route is a simple and quick method to prepare the self-assembled complexes and facilitates isolation and purification. In principle, the self-assembled complex **4** should exhibit novel electrochemical properties, as six ferrocenyl-substituted groups occupy different positions at the vertexes of the octahedral cage molecule. Moreover, the ligand **3** is extremely electron-deficient owing to the triazine groups.^[14] Therefore, the cage complexes provide a nanoscopic hollow environment that can preferentially bind electron-rich guests. This may cause electron transfer from guest molecules to the four triazine ligands.

Results and Discussion

Based on the design strategy, complexes with an octahedral framework can be synthesized by directed self-assembly reactions of four 120° planar tritopic subunits **3** with six 90° ditopic Pd^{II} subunits **1** or **2** in acetone solution. Cage complexes **4** and **5** with roughly octahedral cavity structures are spontaneously formed by simply mixing the six metal precursors (M) and the four organic ligands (L) in a 3:2 ratio. The cage structure can be readily understood by considering a hypothetical octahedron. Six metal precursors occupy every vertex of an octahedron, whereas the four triangular ligands alternatively occupy the eight faces of the octahedron. The ratio of faces to corners must be 4:6 with a total number of 10 subunits to obtain a closed octahedral cage structure.

The formation of a single product, 4, was qualitatively identified by ¹H NMR spectroscopic analysis. In Figure 1 (a), the ¹H NMR spectrum of 4 shows only one set of proton signals, in good agreement with its highly symmetric structure. The peak at $\delta = 9.02$ ppm was assigned to Py H_a (peak a, Py = pyridinyl) and the peak at δ = 8.06 ppm was attributed to the Py H_b of the triazine ligand core of the cage. The peaks c, d and e correspond to the three protons of the phenyl group of the Pd^{II} metal subunit. The proton signals H_f and H_g at $\delta = 4.94$ and 4.85 ppm, respectively, characterized two protons in the ferrocenyl-substituted group. The integration ratio of the seven protons (H_{a-q}) was approximately 24:24:48:24:48:24:24 $(H_a/H_b/H_c/H_d/H_e/H_f/$ H_{g}), in accordance with the stoichiometric ratio 6:4 of 1 and 3. Similar results were obtained for 5. Elemental analysis of 4 and 5 provided further evidence to support the identification of the current cage structures.

The diffusion coefficient is often used to determine the size of molecules,^[15] as the self-diffusion coefficient of a molecule depends not only on the viscosity of the solvent but also the effective size of individual molecule/supramolecule. We carried out ¹H NMR diffusion-ordered spectroscopy (DOSY) experiments for both 4 and 5 in [D₆]acetone solution. In Figure 1 (b), all proton signals of 4 give only one diffusion coefficient at $5.62 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (log D = -8.25). The diameter of 4 was estimated as 3.1 nm based on the Stokes–Einstein equation.^[16] Similarly, complex 5 was





Figure 1. a) ¹H NMR spectrum (600 MHz, [D₆]acetone, 298 K) of 4. Signals a and b denote Py H_a (Py = pyridinyl) and Py H_b of the tritopic ligand; signals c, d, e and f, g denote phenyl and ferrocenyl ring protons, respectively, and b) ¹H DOSY spectrum of 4 (600 MHz, [D₆]acetone, 298 K).

assembled from six 90° Pd^{II}-containing subunits **2** and four tritopic ligand subunits **3**. The diffusion coefficient determined by a DOSY experiment was $5.25 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ (log *D* = -8.28) in [D₆]acetone.

The molecular size of 4 was confirmed directly by AFM (Figure 2), which clearly showed the diameter of 4 was approximately 3–4 nm. The results also revealed the stability of the nanoparticles under AFM conditions. The framework structures of 4 (DFT, B3LYP method) and 5 (PM₆ method) were further studied by theoretical calculations

(Figure S2–3). In the calculations, the optimized geometries of **4** and **5** clearly displayed a highly symmetric octahedral structure. Taking **4** for example, the interior diagonal Pd–Pd distance was calculated to be 1.9 nm and the Pd–Pd distance for the triangular facial windows was 1.4 nm. From a stick model, an approximate diameter of 3.3 nm was derived for the overall size of **4**, and the distance between neighbouring ferrocene units was 2.0 nm (Figure S2). The calculated diameter of **4** was in good agreement with those obtained from the DOSY deduced results and AFM observations.

The single-electron-accepting character of **5** is supported by theoretical calculations. Owing to the rather high symmetry of the structure of **5**, a few of the occupied orbitals near the highest occupied molecular orbital (HOMO) are degenerate. The same situation happens for several unoccupied molecular orbitals near the lowest unoccupied molecular orbital (LUMO). Interestingly, the electronic population densities of the HOMO and LUMO are located in the Pd– bis(triphenylphosphane) part and the tritopic triazine part, respectively (Figures 3 and S4). This phenomenon indicates that the HOMO–LUMO transition leads to an electronically excited state with strong intramolecular charge-transfer (CT) character. Furthermore, several similar CT states



Figure 3. HOMO and LUMO of octahedral cage 5.



Figure 2. AFM images of 4 on mica: a) 3D image, b) 2D image and c) height profile.



should exist in the low excitation energy domain for such systems owing to the orbital degeneracy. As previously suggested by Fujita et al.,^[17] the presence of these low-lying CT states may allow us to perform the photocatalysis of some oxidation/reduction reactions that do not take place in ordinary chemical environments. Meanwhile, we presume that this CT feature of this type of system may also have potential use in artificial photosynthesis.^[18]

Despite extensive efforts, we have not been successful in growing suitable X-ray quality crystals of the complexes. This may be due to the large cavity size of the molecules and the high solvent content of the crystals. However, the physical and spectroscopic data are consistent with the octahedral structures based on our experimental results and theoretical calculations.

The electrochemical properties of the multiferrocene complex 4 were also investigated. Cyclic voltammograms of precursor 1 and complex 4 were recorded in 1.8 and 0.3 mm acetone solutions, respectively, with $0.1 \text{ M} n \text{Bu}_4 \text{NPF}_6$ as supporting electrolyte. The cyclic voltammograms of 1 exhibited typical reversible redox curves from 0.2 to 1.6 V, as shown in Figure S1. The cyclic voltammograms of 4 showed a pair of quasireversible redox peaks, which indicated that no interaction existed among the different ferrocene redox centres (Figure 4). The potential difference (ΔE_p) between the oxidation peak potentials (E_{pa}) and reduction peak potentials (E_{pc}) was 96 ± 9 mV, which is larger than the theoretical value for an ideal quasireversible redox system (59 mV at 298 K) owing to the resistance of the solution.^[19] Meanwhile, the oxidation and reduction peak currents of 4 increased linearly with respect to the square root of the sweep rates from 25 to 200 mV s⁻¹. The oxidation and reduction peak potentials were both slightly shifted with higher sweep rates, which indicated the existence of a diffusion-controlled quasireversible redox process. Cyclic voltammograms of 4 displayed a considerably broad voltammetric peak, which was probably due to the simultaneous statistical nature of the multielectron transfer processes, in accordance with previously reported ones.^[20] No decomposition of the octahedral complex during these redox pro-



Figure 4. Cyclic voltammetry of 4 at different scan rates (25–200 mV s⁻¹) at a 3 mm diameter glassy carbon working electrode in 0.3 mM acetone solution containing 0.1 M nBu_4NPF_6 , vs. Ag/AgCl.

cesses was observed, as clarified by the ¹H NMR spectra of **4** before and after the electrochemical reactions. As proposed by Stang et al.,^[21] electrochemical reversibility indicates that fast electron transfer processes occur among the six peripheral redox sites. Such fast heterogeneous electron transfer processes were caused by fast rotation or electron hopping between the different subunits. The combination of ferrocene functional moieties with transition metal complexes offered a marvellous chance to link the chemistry of ferrocenes with supramolecular self-assembly, thus opening new families of compounds to possible redox processes. These novel assembly systems with multiredox groups could potentially be used as multielectron catalysts and sensors.

Conclusions

We have prepared nanoscale octahedral structures through coordination self-assembly in a common organic phase system. The coordination self-assembly allows for the precise control of the shape, size and location of multiple functional groups. When functional groups (such as ferrocenyl-substituted groups) are attached onto the vertices of Pd^{II} metal subunits, such self-assembled complexes exhibit interesting multiredox properties. Meanwhile, the functional units retain their functional fidelity, and the large discrete 3D supramolecular hollow structure provides an ideal cavity for molecular recognition, inclusion phenomena and catalysis. We are currently exploring the possibility of oligopeptide encapsulation in the octahedral structures, in which functional groups are expected to provide a new means to characterize electron transfer from guest molecules to the triazine ligands. We envision that the addition of functional moieties and encapsulated moieties to the periphery and the interior of the nanocage, respectively, will lead to many new materials with special electrochemical or photochemical applications, such as multi-electron redox catalysts, electrode modifiers and sensors.

Experimental Section

Material: Reagents were purchased from TCI Co. Ltd., WAKO Pure Chemical Industries Ltd. and Sigma–Aldrich Co. Dichloromethane and acetone were distilled from calcium hydride prior to use. All other chemicals were of reagent grade and were used without any further purification.

[Pd(dppf)(OTf)₂] (1): A Schlenk flask was charged with [Pd(dppf)-Cl₂] (225.1 mg, 0.307 mmol) and anhydrous CH₂Cl₂ (20 mL) to give a dark red solution. To this solution was added AgOTf (236.6 mg, 0.921 mmol), and the mixture was stirred at room temperature for 8 h in darkness. The white precipitate was removed by filtration, and the filtrate was reduced in volume to 3 mL. After the addition of diethyl ether, the green product that precipitated was collected by filtration, washed with diethyl ether and dried in vacuo, yield 268.3 mg (91%), dark green solid. ¹H NMR (600 MHz, [D₆]acetone, 298 K): $\delta = 8.01$ (m, 8 H, Ph H_o), 7.82 (m, 4 H, Ph H_p), 7.66 (m, 8 H, Ph H_m), 4.89 (s, 2 H, ferrocene H_a), 4.84 (s, 2 H, ferrocene H_β) ppm. DEPTQ ¹³C NMR (150 MHz, [D₆]acetone, 298 K): $\delta = 135.1$ (CH), 134.5 (CH), 130.6 (CH), 128.9



(C), 122.6 (C), 79.7 (CH), 77.4 (CH), 69.9 (C) ppm. $C_{36}H_{28}F_6FeO_6P_2PdS_2$ (958.92): calcd. C 43.46, H 3.24, S 6.45; found C 43.52, H 3.31, S 6.49.

[Pd(PPh₃)(OTf)₂] (2): A Schlenk flask was charged with [Pd(PPh₃)-Cl₂] (212.3 mg, 0.302 mmol) and anhydrous CH₂Cl₂ (20 mL) to give a yellow solution. To this solution was added AgOTf (226.5 mg, 0.882 mmol), and the mixture was stirred at room temperature for 2 h. The white precipitate was removed by filtration, and the filtrate was reduced in volume to 3 mL. After the addition of diethyl ether, the brown precipitate was collected by filtration, washed with diethyl ether and dried in vacuo, yield 261.3 mg (93%), brown solid. ¹H NMR (600 MHz, [D₆]acetone, 298 K): δ = 7.72 (m, 18 H, H_o and H_p), 7.51 (m, 12 H, H_m) ppm. DEPTQ ¹³C NMR (150 MHz, [D₆]acetone, 298 K): δ = 135.6 (CH), 134.3 (CH), 130.5 (CH), 125.7 (C), 125.3 (C), 120.6 (C) ppm. C₃₈H₃₀F₆O₆P₂PdS₂ (929.11): calcd. C 49.12, H 3.25, S 6.90; found C 49.16, H 3.31, S 6.97.

Cage 4: 2,4,6-Tris(4-pyridyl)-1,3,5-triazine 3 (9.9 mg, 0.032 mmol) was suspended in an acetone solution (30 mL) of [Pd(dppf)- $(OTf)_2$ (1, 45.2 mg, 0.047 mmol), and the mixture was stirred at room temperature for 30 min; the solution gradually turned clear pink. After the solvent was evaporated, the resulting residue was washed with diethyl ether three times and dried in vacuo to yield 4 (47.3 mg) as a pink solid in 87% yield. ¹H NMR (600 MHz, $[D_6]$ acetone, 298 K): δ = 9.02 (d, J = 4.2 Hz, 24 H, pyridyl H_a), 8.06 $(d, J = 6.0 \text{ Hz}, 24 \text{ H}, \text{ pyridyl } H_{\beta}), 7.99 \text{ (m, 48 H, Ph } H_{o}), 7.72 \text{ (m,})$ 24 H, Ph H_p), 7.64 (m, 48 H, Ph H_m), 4.94 (s, 24 H, ferrocene H_a), 4.85 (s, 24 H, ferrocene H_{β}) ppm. Diffusion coefficient ([D₆]acetone, 298 K): $D = 5.62 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$. DEPTQ ¹³C NMR (150 MHz, $[D_6]$ acetone, 298 K): $\delta = 168.7$ (C), 151.6 (CH), 144.3 (C), 134.3 (CH), 133.1 (CH), 130.0 (CH), 127.5 (C), 124.7 (CH), 120.3 (C), 77.3 (CH), 76.0 (CH), 69.0 (C) ppm. C₂₈₈H₂₁₆F₃₆Fe₆N₂₄₋ O₃₆P₁₂Pd₆S₁₂ (7002.83): calcd. C 49.39, H 3.11, N 4.80, S 5.49; found C 49.46, H 3.04, N 4.85, S 5.43.

Cage 5: 2,4,6-Tris(4-pyridyl)-1,3,5-triazine 3 (8.1 mg, 0.026 mmol) was suspended in an acetone solution (30 mL) of [Pd(PPh₃)-(OTf)₂] 2 (35.4 mg, 0.038 mmol), and the mixture was stirred at room temperature for 2 h; the solution gradually turned colourless. After the solvent was evaporated, the resulting residue was washed with diethyl ether three times and dried in vacuo to yield 5 (36.0 mg) as a white solid in 92% yield. ¹H NMR (600 MHz, [D₆]acetone, 298 K): $\delta = 9.26$ (d, J = 4.2 Hz, 24 H, pyridyl H_a), 8.13 $(d, J = 6.0 \text{ Hz}, 24 \text{ H}, \text{ pyridyl } H_{\beta}), 7.82 \text{ (m}, 72 \text{ H}, \text{ Ph } H_{o}), 7.61 \text{ (m},$ 36 H, Ph H_p), 7.48 (m, 72 H, Ph H_m) ppm. Diffusion coefficient ([D₆]acetone, 298 K): $D = 5.25 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$. DEPTQ ¹³C NMR (150 MHz, [D₆]acetone, 298 K): $\delta = 169.6$ (C), 152.6 (CH), 145.0 (C), 135.4 (CH), 133.6 (CH), 130.6 (CH), 126.3 (C), 125.9 (C), 125.6 (CH), 123.4 (C) ppm. $C_{300}H_{228}F_{36}N_{24}O_{36}P_{12}Pd_6S_{12}$ (6823.97): calcd. C 52.80, H 3.37, N 4.93, S 5.64; found C 52.89, H 3.45, N 4.95, S 5.56.

Structure Characterization: Various NMR (¹H NMR, DEPTQ NMR) spectra were recorded with a Bruker DRX-600 (600 MHz) spectrometer. Tetramethylsilane (CDCl₃ solution) in a capillary was used as an external standard. The DOSY NMR spectra were acquired with the standard pulse program from Bruker Topspin software, ledbpgp2s, with a stimulated echo and longitudinal eddy current delay, with bipolar sine-shaped gradient pulses and two spoiling gradients. DOSY NMR spectra were recorded with 32000 time domain data points in the t_2 dimension and 16 t_1 increments, 16 transients for each t_1 increment and a relaxation delay of 1 s. Elemental analysis was performed with a vario EL cube instrument. The molecular structures of the cage complexes **4** and **5** were ob-

tained by electronic-structure calculations with the Gaussian package.^[22] As the current systems are extremely large, the semi-empirical PM₆ method was employed in the calculations of complex **5**. However, complex **4**, which contains ferrocene groups, cannot be described correctly at the PM₆ level, thus we had to use the DFT B3LYP level of theory and perform the calculations on a simplified model system.

Electrochemical Measurements: Electrochemical measurements were made with a CHI 660D System. The working electrode was a 3 mm diameter glassy carbon electrode, a platinum wire as counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode. All electrochemical experiments were performed in acetone solutions with nBu_4NPF_6 (0.1 M) as supporting electrolyte; oxygen was removed from the solutions by bubbling through high-purity argon before the experiments. The concentration of redox molecules in solution was 1.8 mM for 1 and 0.3 mM for4.

Supporting Information (see footnote on the first page of this article): Cyclic voltammograms and molecular modelling procedures are presented.

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