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Tetrahedron Letters
Tetrahedron Letters 47 (2006) 8847–8850

Self-assembly of octacyano-biscavitand by metal ligand interaction: incorporation of container unit in polymer back bone

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Received 7 September 2006; accepted 12 October 2006

Abstract—Octacyano-biscavitand **2** was synthesized and the formation of its self-assembled oligomeric coordination molecular capsule **4** with Pd(dppp)OTf_2 was studied by ^{1}H NMR, PGSE NMR, and SEM. Oligomeric capsule **4** having container units in the backbone was chopped down to hetero-coupled biscapsules **5** by pyridinocavitand **3**.

The efficiency and the architectural beauty of the molecular self-assemblies are quite familiar in biological as well as artificial systems. Self-assembled supramolecular polymers are formed with the well-designed monomer units to be held reversibly by hydrogen bonds,[1] solvophobic π–π stacking interactions,[2] or metal–ion coordination.[3]

Metal coordination has been used to prepare a wide range of supramolecular complexes with geometries varying in complexity from simple cyclic dimers to catenanes, helicates, and cages with intricate geometries.[4] Self-assemblies of coordination cage compounds of two tetracyano cavitand lignads[5] or two tetrapyridyl cavitands[6] were reported. Recently, Kobayashi et al. reported on the general properties of self-assemblies of coordination homo or hetero cage compounds composed of tetrakis(4-cyanophenyl)-cavitand, tetrakis(4-pyridyl)-cavitand, or tetrakis(4-pyridylethynyl)-cavitand connected through four Pd(II) or Pt(II) square-planar complexes.[7]

When octacyanobiscavitands which consist of two tetracyanocavitands connected covalently through their feet were self-assembled by metal coordination, a new kind of polymeric systems having container units in the backbone could be formed.

Hexadecol, which consists of two octols connected through a biphenyl foot in a back-to-back fashion, was synthesized by heterogeneous condensation among resorcinol, octanal, and 4,4′-bisformylbiphenyl.[8a] Hexadecol was reacted with NBS and then with CH_2BrCl in a mixture of K_2CO_3 and DMF to afford an octabromobiscavitand **1**.[8b] Under the Pd(0)-catalyzed Suzuki coupling reaction between **1** and 4-cyanobenzeneboronic acid in a mixture of THF and aqueous KF solution (2 M),[9] octacyano-biscavitand **2** was obtained in 56% yield. Octacyano-biscavitand **2** was fully characterized by ^{1}H NMR, MALDI-TOF-MS, and elemental analysis (Scheme 1).

Square-planar *cis*-Pd(dppp)OTf_2 was prepared by the reaction of Pd(dppp)Cl_2 with AgOTf (dppp = 1,3-bis diphenylphophinopropan, OTf = triflate).[10] Oligomeric coordination molecular capsule **4** was formed by simply mixing **2** with Pd(dppp)OTf_2 in a 1:4 molar ratio at room temperature in nonpolar solvents such as CH_2Cl_2 or $CHCl_3$ (Scheme 2).

Metal coordination of biscavitand **2** with Pd(dppp)OTf_2 was followed by ^{1}H NMR spectroscopy in CD_2Cl_2 at 25 °C (Fig. 1 and Table 1). When metal salt Pd(dppp)OTf_2 was slowly added to the solution of biscavitand **2**, the ^{1}H NMR spectrum shows the peaks of outer (5.25 ppm) and inner (4.13 ppm) dioxymethylene hydrogens upfield (5.07 ppm) and downfield (4.22 ppm) shifted, respectively, until the metal-to-ligand molar ratio reaches to 4:1 to complete the forma-

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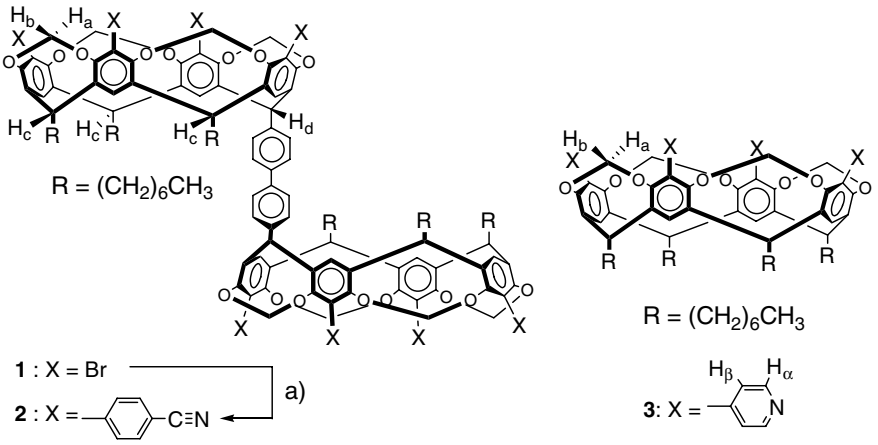
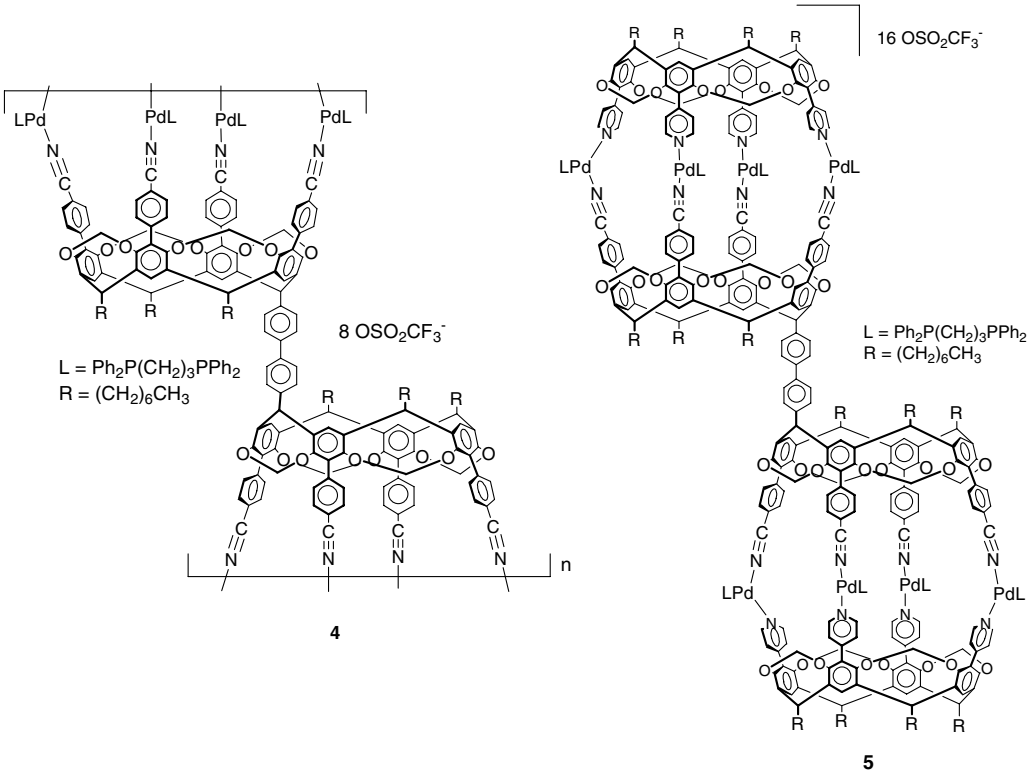
doi:10.1016/j.tetlet.2006.10.058



Scheme 1. (a) 4-Cyanobenzenboronic acid, $Pd(PPh_3)_4$, THF, 2 M KF, EtOH, reflux, 56%.



Scheme 2.

tion of oligomer **4**. Excess addition of metal salt has little influence on the NMR spectra. Also the peaks of methine protons (6.54, 4.83 ppm) of biscavitand **2** shifted upfield upon the formation of oligomer **4** by metal–ligand interaction (6.45 and 4.75 ppm).

Such an self-assembly of biscavitand **2** to oligomer **4** by metal coordination was disrupted by adding 2 equiv of tetra(4-pyridyl)-cavitand **3**[7] and 4 equiv of Pd(dppp)-OTf_2 as shown in Figure 1c. The mixture of **2**, **3**, and Pd(dppp)OTf_2 in 1:2:8 ratio allowed the formation of self-assembled hetero-coupled bis-capsule **5** due to the stronger metal affinity of pyridyl ligand as well as the low stability of homo-capsule of pyridinocavitand **3**.[7a]

The peaks of α- and β-protons of *p*-pyridyl group of cavitand **3** shifted upon the formation of biscapsule **5** from 8.56 and 6.94 ppm to 8.85 and 6.81 ppm, respectively. Also the outer and inner protons of dioxymethylene and methine protons cavitand **3** shifted from 5.10, 4.16, and 4.83 ppm to 5.61, 4.31, and 4.68 ppm, respectively, upon the formation of biscapsule **5**. The chemical shift of outer dioxymethylene proton of unit **2** in **5** (4.88 ppm) moved further upfield compared to that in **4** (5.07 ppm).

The ^{31}P NMR of **4** showed a sharp singlet peak at 16 ppm, which indicated the equivalency of all phosphorus atoms, thus confirming the simple oligomeric struc-

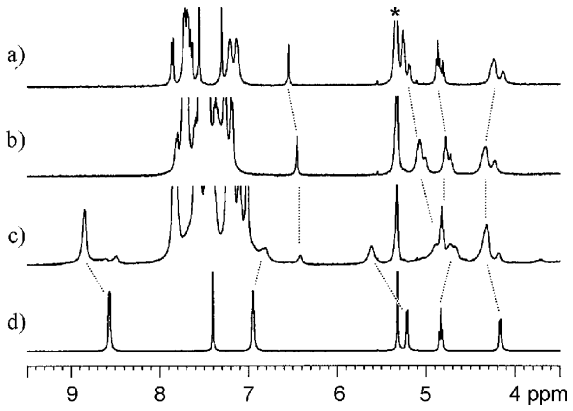
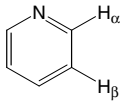


Figure 1. Partial ^{1}H NMR spectra ([**2**] = 1.5 mM in CD_2Cl_2, 400 MHz, 298 K): (a) **2** alone; (b) self-assembled oligocapsule **4**: [**2**] = 1.5 mM and [Pd(dppp)OTf$_2$] = 6.0 mM, (c) self-assembled Biscapsule **5**: [**2**] = 1.5 mM, [Pd(dppp)OTf$_2$] = 12.0 mM and [**3**] = 3.0 mM; (d) **3** alone.

Table 1. ^{1}H NMR chemical shift changes of selected protons in cavitands. (400 MHz, 298 K, CD_2Cl_2)

		2	**4**	**2** in **5**	**3** in **5**	**3**
Inner OCH_aO		4.13	5.07	4.88	4.31	4.16
Methine	H_c	4.83	4.75	4.82	4.68	4.83
	H_d	6.53	6.45	6.41		
Outer OCH_bO		5.25	4.22	[a]	5.61	5.10
	H_α	—	—	—	8.85	8.56
	H_β	—	—	—	6.81	6.94

[a] Overlapped by other peaks.

ture of **4**. Whereas biscapsule **5** showed new two doublet peaks at 9.37 and 6.31 ppm with $^3J_{pp} = 27.0$ Hz due to the dppp (1,3-bis(diphenylphosphino)propane) desymmetrized by the hetero-coupled coordination capsule. The ^{19}F NMR of **4** and **5** showed a single peak at −80 ppm, indicating the free access of TfO^- to the cavity.[3b,c,4a]

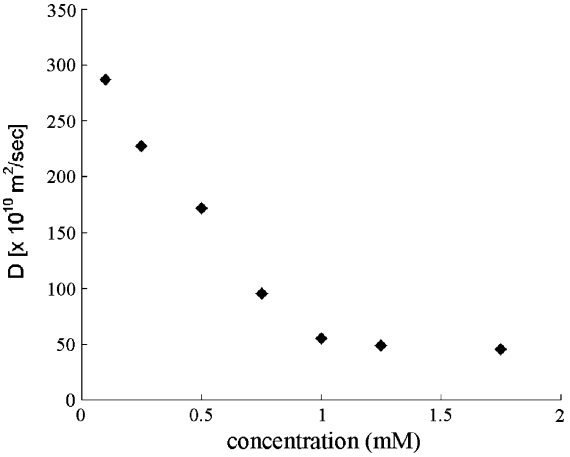


Figure 2. The concentration dependence of diffusion coefficients ($\times 10^{10}$) of octacyano-biscavitand **2**–Pd(dppp)OTf$_2$ in $CDCl_3$ at 298 K.

The pulse-field gradient spin-echo (PGSE) NMR technique[11] was used to measure the diffusion coefficients of oligomeric **4** in $CDCl_3$ at 298 K. The diffusion coefficients show notable change with concentration from 0.1 mM to 1.0 mM, as shown in Figure 2. The concentration-dependent decreases in diffusion coefficients indicate that coordinated oligomer **4** becomes larger as the concentration increases. At concentration of 1.0 mM, the volume of **4** is approximately 141-fold greater than that at 0.1 mM.

Scanning electron microscope (SEM) was used to observe the microscopic structure of oligomeric capsule **4** (Fig. 3). The electron microscopic picture of the sample formed from biscavitand **2** with Pd(dppp)OTf$_2$ in $CHCl_3$ revealed that oligomeric capsule **4** forms fibrous aggregates in a concentration range of 0.1–0.05 mM. Under the lower concentration (<0.01 mM), these fibrous aggregates disappeared, and only numerous dots were observed.

In conclusion, new octacyano-biscavitand **2** was synthesized and characterized. The formation of their oligomeric coordination molecular capsule **4** was studied by ^{1}H NMR, PGSE NMR, and SEM. Oligomeric capsule **4** was transformed to hetero-coupled biscapsule **5** by pyridinocavitand **3**, which is a way of manipulation of coordinated polymeric container supramolecules.

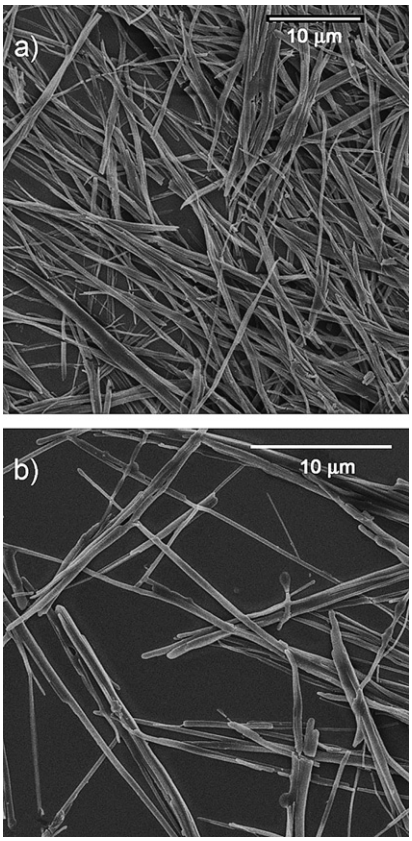


Figure 3. SEM images of **4**. (a) 0.5 mM, (b) 0.1 mM in $CHCl_3$, scale bar = 10 μm.

Acknowledgments

This work was supported by Korea Research Foundation Grants (KRF-2005-005-J01102) and Center for Bioactive Molecular Hybrids (Yonsei University, 2006).

Supplementary data

General detailed experimental procedures of **1**–**3** and NMR spectra of **1**–**5**, and 3D structure of **2**, **4**, and **5**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.058.

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