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Molecular Engineering. Part 14: Synthesis and Self-Assemblies of a Back-to-back Connected Octacyanobiscavitand

C. Ihm[a]; K. Paek[a]
[a] Department of Chemistry and CAMDRC, Soongsil University, Seoul, South Korea

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Molecular Engineering. Part 14: Synthesis and Self-Assemblies of a Back-to-back Connected Octacyanobiscavitand

C. IHM and K. PAEK*

Department of Chemistry and CAMDRC, Soongsil University, Seoul 156-743, South Korea

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Octacyano-biscavitand 4, which consists of two tetracyanocavitands back-to-back connected to each other through a biphenyl unit, was synthesized. The formation of self-assembled coordination oligocapsule 10 of biscavitand 4 and Pd(dppp)OTf$_2$ was studied by ^{1}H NMR, ^{31}P NMR, PGSE NMR, and SEM. Oligocapsule 10, having container units in the backbone, was chopped down to hetero-coupled biscapsule 11 by pyridinocavitand 9 which has a stronger binding affinity to Pd(II) without forming a homocapsule.

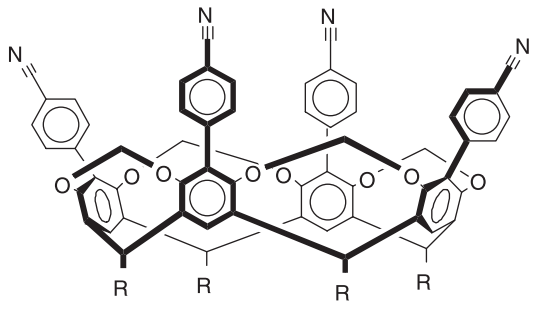
Keywords: Cyanocavitand; Octacyanobiscavitand; Self-assembly; Metal coordination; Oligocapsule

INTRODUCTION

Octols obtained from the condensation reactions between resorcinols (resorcinol, 2-methylresorcinol, or pyrogallol) and aldehydes (alkyl or arylaldehyde) are versatile molecular vessels for the various artificial molecular receptors. They have been characterized as molecular receptors as themselves [1–3] or as distinct aggregates [4–6] and also modified to covalently confined container molecules [7–10] and supramolecular systems self-assembled by non-covalent interactions [11–15].

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 [16–18], solvophobic $\pi-\pi$ stacking interactions [19–21], or metal–ion coordination [22–24].

Metal coordination has been used to prepare a wide range of supramolecular complexes from simple cyclic dimers to catenanes, helicates, and cages with intricate geometries [25,26]. 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 **1**, tetrakis(4-pyridyl)-cavitand **2**, or tetrakis(4-pyridylethynyl)-cavitand connected through four Pd(II) or Pt(II) square-planar complexes [27,28].



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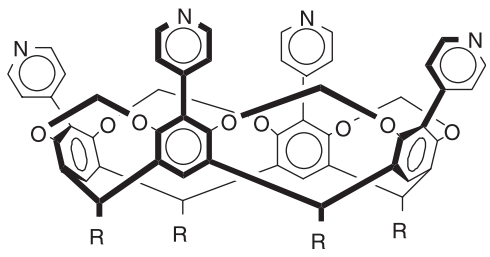

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*Corresponding author. E-mail: kpaek@ssu.ac.kr

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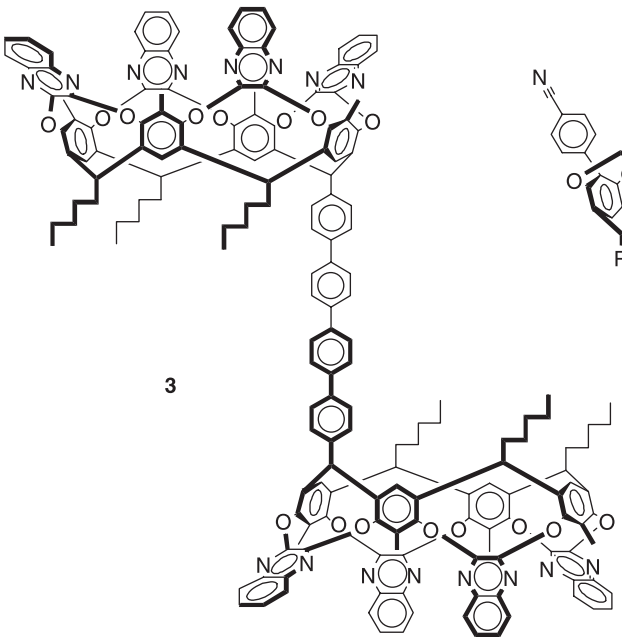
Recently bisvelcrand **3** was reported to form a new kind of polymer (oligobisvelcraplex) formed only by solvophobic π−π stacking interaction [12]. Octacyanobiscavitand **4** which consists of two tetracyanocavitands connected covalently through their feet in back-to-back fashion was obtained [29] and its self-assemblies by metal coordination, a new kind of supramolecular system having reversible container units in its backbone, was characterized.



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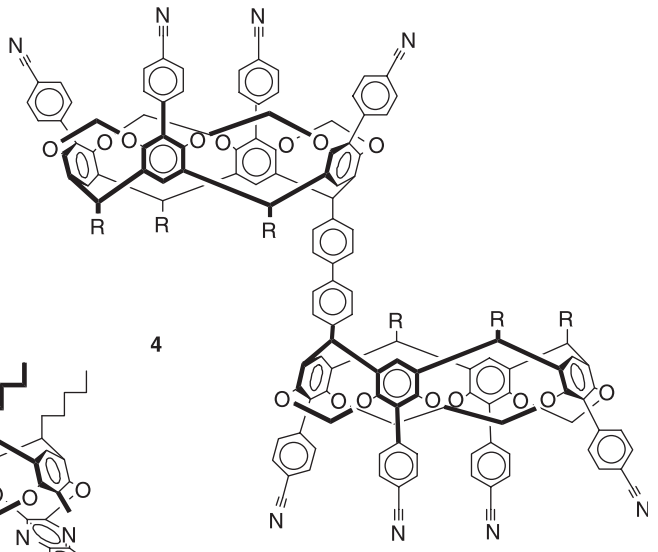

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RESULTS AND DISCUSSIONS

Synthesis of Octacyanobiscavitand 4

Octol **5** and hexadecol **6** which consists of two octols connected through a biphenyl bridge in a back-to-back fashion were synthesized by heterogeneous condensation among resorcinol, octanal, and 4,4′-bisformylbiphenyl (Scheme 1) [30]. Octol **5** and hexadecol **6** were reacted with NBS and then with CH_2BrCl in a mixture of K_2CO_3 and DMF to afford a tetrabromocavitand **7** and octabromo-biscavitand **8** in 54% and 35% yields for two steps, respectively [31] (Scheme 1).

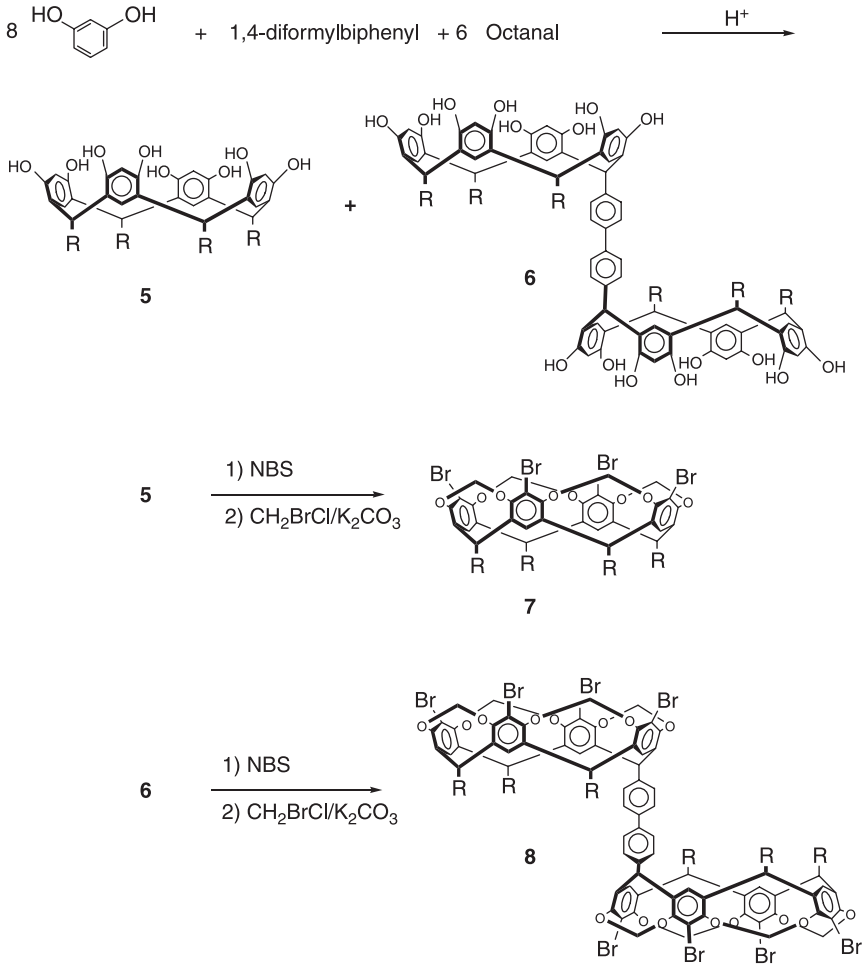
Under the Pd(0)-catalyzed Suzuki coupling reaction between **8** and *p*-cyanobenzeneboronic acid in a mixture of THF and aqueous KF solution (2M) [32], octacyanobiscavitand **4** was obtained in 56% yield [29]. Octacyanobiscavitand **4** was fully characterized by ^{1}H NMR, MALDI-TOF-MS and elemental analysis. Tetrakispyridinocavitand **9** was obtained by the known procedure [27].

Figure 1 compares ^{1}H NMR spectra of octabromobiscavitand **8** and octacyanobiscavitand **4**. There are two kinds of *p*-cyanophenyl groups for biscavitand **4**. The peaks of four *p*-cyanophenyl groups remote from biphenyl bridge are overlapped with those of H_f peaks at 7.68–7.59 ppm, but the two doublets of other four *p*-cyanophenyl groups close to biphenyl bridge appeared at 7.22 ppm and 7.14 ppm ($J = 8.0$ Hz). Also there are two kinds of aryl hydrogens except those of the biphenyl unit, which appeared at 6.93 ppm and 7.18 ppm for biscavitand **8** and 7.27 ppm and 7.52 ppm for biscavitand **4**. The peak of H_e appeared at 7.72 ppm ($J = 8.0$ Hz) for biscavitand **8** and at 7.82 ppm ($J = 8.4$ Hz) for biscavitand **4**. All the aryl peaks of biscavitand **4** downfield-shifted compared to those of biscavitand **8**. But, interestingly, the multiplet of outer hydrogens of dioxymethylene units of biscavitand **4** upfield-shifted from 6.05–5.95 ppm of biscavitand **8** to 5.31–5.22 ppm. Also those peaks of corresponding inner hydrogens of biscavitand **4** upfield-shifted to 4.28, 4.25, and 4.15 ppm from the multiplet at 4.37–4.54 ppm of biscavitand **8**. It is presumable that *p*-cyanophenyl groups form a stronger magnetically shielding zone to outer hydrogens of dioxymethylene units compared to the corresponding inner hydrogens.

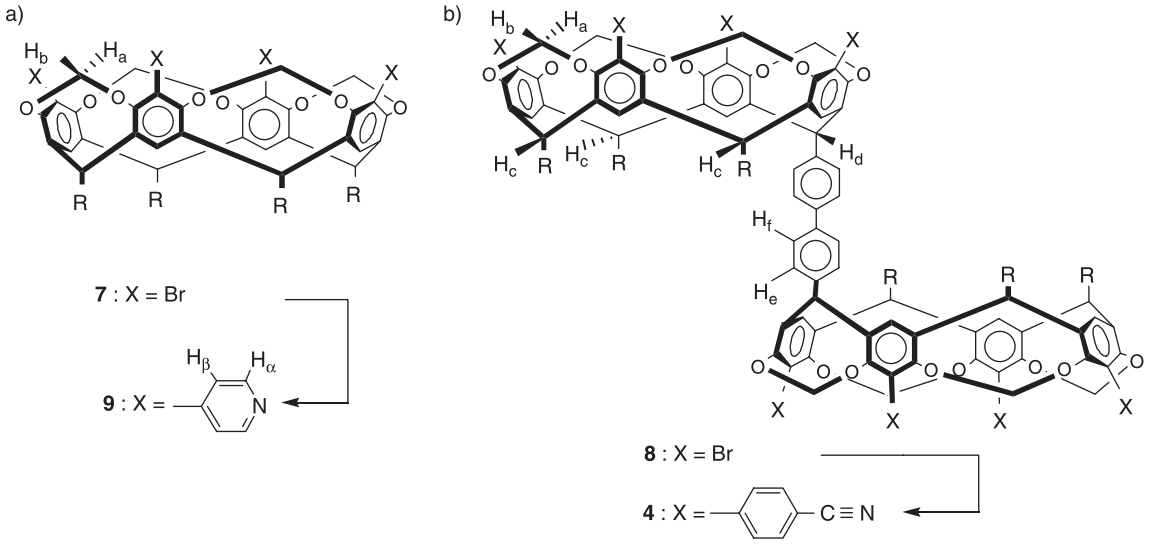
The top and side stereoviews of energy-minimized octacyanobiscavitand **4** in Fig. 2 show the defined two deep-cavities connected by biphenyl units in back-to-back mode.

Metal-coordinated Self-assemblies 10 and 11 of Octacyanobiscavitand 4

Square-planar *cis*-Pd(dppp)OTf_2 was prepared by the reaction of Pd(dppp)Cl_2 with AgOTf (dppp = 1,3-bis (diphenylphophino)propane, OTf = triflate) [33–35].



SCHEME 1 Synthesis of tetrabromocavitnad **7** and octabromobiscavitand **8** (R = Heptyl).



SCHEME 2 Synthesis of Biscavitand **4** and Cavitand **9** (R = Heptyl); a) pyridine-4-boronic acid, $Pd(PPh_3)_4$, THF, 2M KF, EtOH, reflux, 58%, b) 4-cyanobenzenboronic acid, $Pd(PPh_3)_4$, THF, 2M KF, EtOH, reflux, 56%.

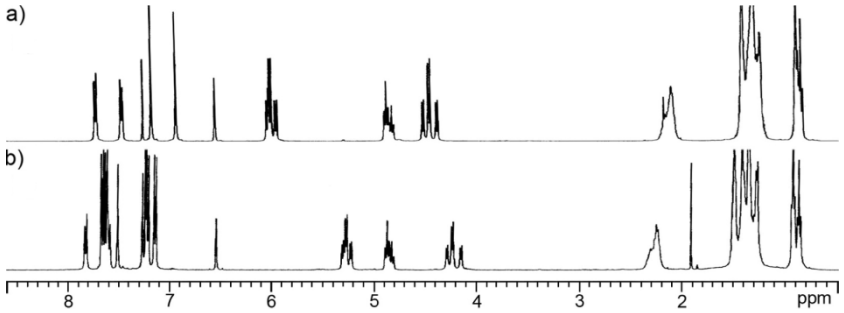


FIGURE 1 ^{1}H NMR spectra ($CDCl_3$, 400.1 MHz, 298 K): a) Octabromobiscavitand **8** and b) Octacyanobiscavitand **4**.

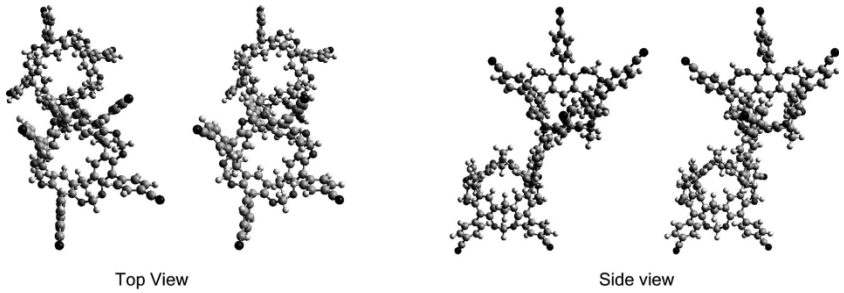
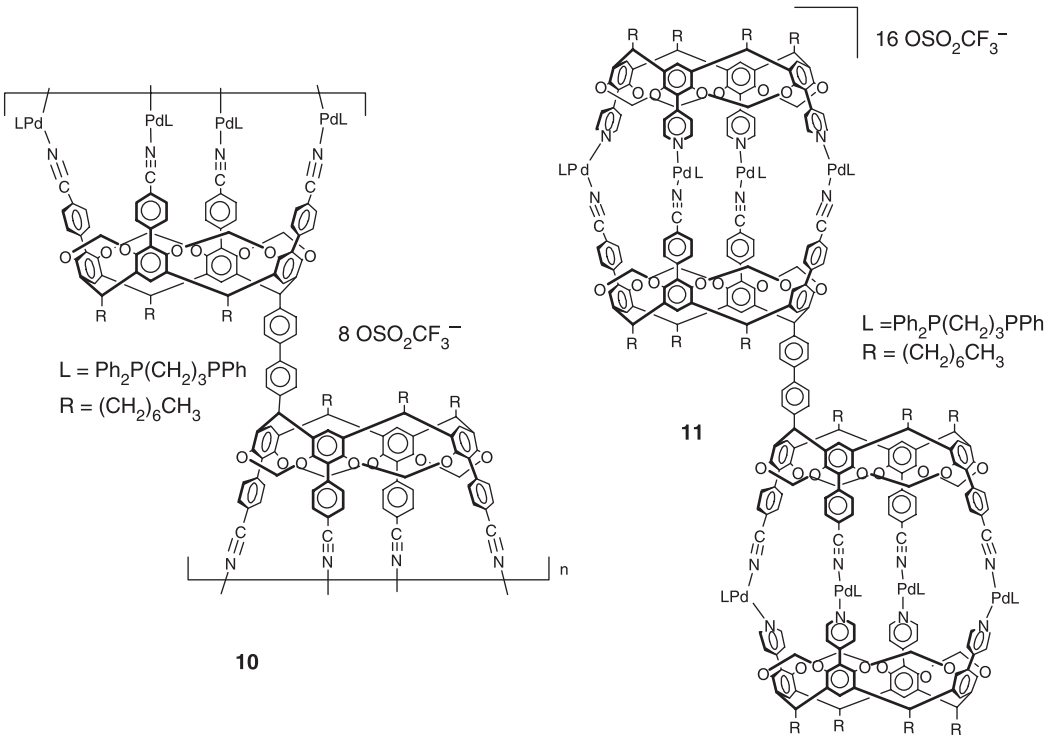


FIGURE 2 Stereo view of **4** by Hyperchem 7.5® (MM + force field; the heptyl feet groups have been substituted by methyl groups for clarity).

Oligomeric coordination molecular capsule **10** was formed by simply mixing biscavitand **4** with $Pd(dppp)OTf_2$ in a 1:4 molar ratio at room temperature in the nonpolar solvents such as CH_2Cl_2 or $CHCl_3$.

Metal coordination of biscavitand **4** with $Pd(dppp)OTf_2$ was followed by ^{1}H NMR spectroscopy in CD_2Cl_2 at 25°C (Figs. 3 and 4 and Table I). When metal salt $Pd(dppp)OTf_2$ was slowly added



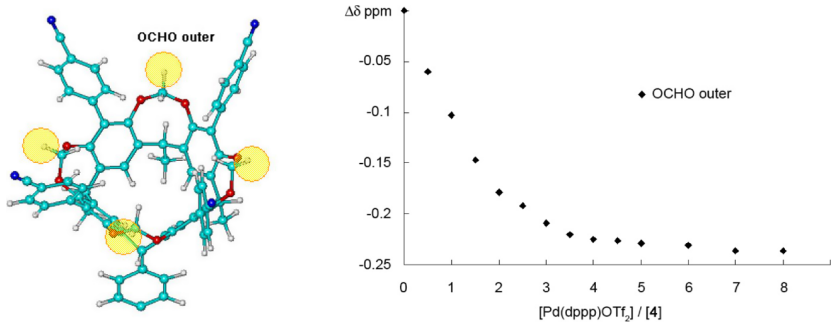


FIGURE 3 Chemical shift change of outer OCHO protons (H_b) of biscavitand **4** by the addition of $Pd(dppp)OTf_2$. [**4**] = 1 mM in $CDCl_3$, 400 MHz, 298 K.

to the solution of biscavitand **4**, the ^1H 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 4:1 to complete the formation of oligomer **10** (Fig. 3). Excess addition of metal salt has little influence on the NMR spectra. Also the peaks of methine protons (6.54 ppm and 4.83 ppm) of biscavitand **2** shifted upfield upon the formation of oligomer **10** by metal–ligand interaction (6.45 ppm and 4.75 ppm).

Such a self-assembly of biscavitand **4** to oligomer **10** by metal coordination was disrupted by adding two equivalents of tetra(4-pyridyl)-cavitand **9** and four equivalents of $Pd(dppp)OTf_2$ as shown in Fig. 4c. The mixture of **4**, **9**, and $Pd(dppp)OTf_2$ in 1:2:8 ratio allowed the formation of self-assembled hetero-coupled bis-capsule **11** due to the stronger metal affinity of the pyridyl ligand as well as the low stability of homo-capsule of pyridinocavitand **9** [27]. The peaks of α- and β- protons of *p*-pyridyl group of cavitand **9** shifted upon the formation of biscapsule **11** from 8.56 ppm and 6.94 ppm to 8.85 ppm and 6.81 ppm, respectively. Also the outer and inner

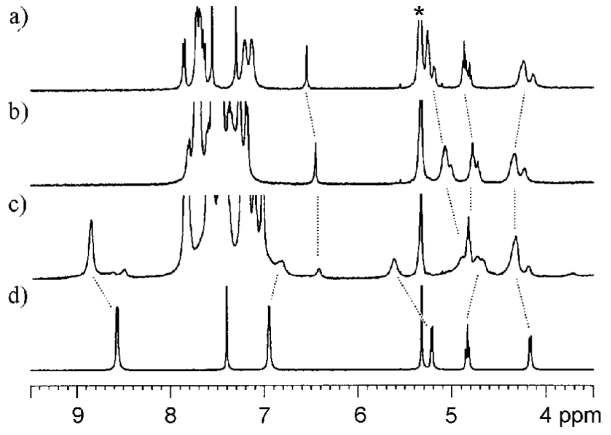


FIGURE 4 Partial ^1H NMR spectra ([**4**] = 1.5 mM in CD_2Cl_2, 400 MHz, 298 K): (a) **4** alone, (b) self-assembled oligocapsule [**10**]:[**4**] = 1.5 mM and $[Pd(dppp)OTf_2]$ = 6.0 mM, (c) self-assembled Biscapsule [**11**]: [**4**] = 1.5 mM, $[Pd(dppp)OTf_2]$ = 12.0 mM and [**9**] = 3.0 mM, (d) **9** alone.

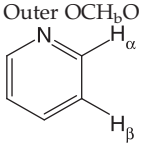
protons of dioxyemthylene and methine protons cavitand **9** shifted from 5.10, 4.16 and 4.83 ppm to 5.61, 4.31 and 4.68 ppm, respectively, upon the formation of biscapsule **11**. The chemical shift of outer dioxymethylene proton of biscavitand **4** in **11** (4.88 ppm) moved further upfield compared to that in **10** (5.07 ppm).

Figures 5 and 6 show the energy-minimized structures of homo-assembled oligocapsule **10** and hetero-assembled biscapsule **11**. Oligocapsule **10** consists of regular container units, which have rather large portals, in its backbone (Fig. 5). Biscapsule **11** consists of two container units connected by biphenyl unit, which have smaller portals compared to those of oligocapsule **10** due to the shorter ligands of tetrakispyridinocavitand **9**.

The ^{31}P NMR of oligocapsule **10** showed a sharp singlet peak at 16 ppm, which indicated the equivalency of all phosphorus atoms, thus confirming its simple oligomeric structure. Whereas biscapsule **11** showed two new doublet peaks at 9.37 ppm 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 **10** and **11** showed a single peak at −80 ppm, indicating the free access of TfO^- to the cavity [23–25].

The pulse-field gradient spin-echo (PGSE) NMR technique [36–39] was used to measure the diffusion coefficients of oligomeric **10** in $CDCl_3$ at 298 K.

TABLE I ^1H NMR chemical shift changes of selected protons in cavitands (400 MHz, 298 K, CD_2Cl_2)

		4	**10**	**4** in **11**	**9** in **11**	**9**
Inner OCH_aO		4.13	4.22	4.31	4.31	4.16
Methane	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	5.07	4.88	5.61	5.10
	H_α	–	–	–	8.85	8.56
	H_β	–	–	–	6.81	6.94

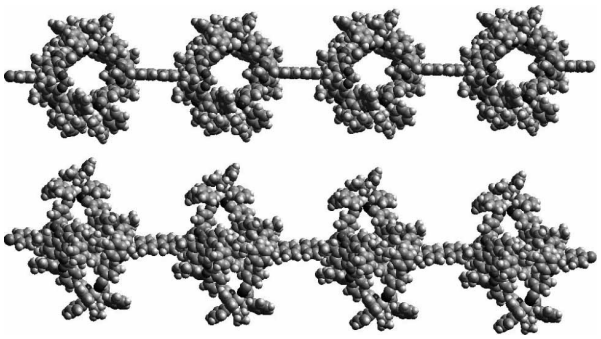


FIGURE 5 Energy minimized structure of homo-coupled coordination molecular oligocapsule **10** by Hyperchem 7.5® (MM + force field; the heptyl feet groups have been substituted by methyl groups for clarity).

The diffusion coefficients show notable change with concentration from 0.1 mM to 1.0 mM, as shown in Fig. 7. The concentration-dependent decreases in diffusion coefficients indicate that coordinated oligomer **10** becomes larger as the concentration increases. At concentrations of 1.0 mM, the volume of **10** is approximately 141 fold greater than that at 0.1 mM.

FE-SEM (Field Emission Scanning Electron Microsope, JEOL JSM-6700F) was used to observe the microscopic structure of oligomeric capsule **10** (Fig. 8). The electron microscopic picture of the sample formed from biscavitand **4** with Pd(dppp)OTf_2 in $CHCl_3$ revealed that oligomeric capsule **10** 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 **4** was synthesized and characterized. The formation of their oligomeric coordination molecular capsule **10** was studied by ^{1}H NMR, ^{31}P NMR, PGSE NMR, and SEM. Oligomeric capsule **10** was transformed to hetero-coupled biscapsule **11** by pyridinocavitand **9**, which is a way of engineering coordinated polymeric container supramolecules.

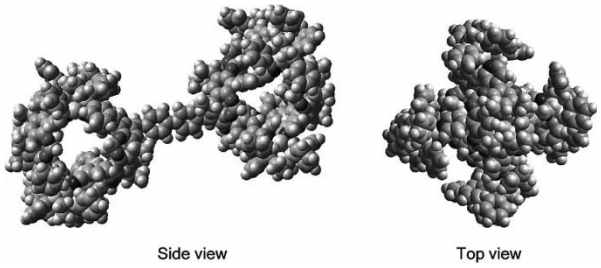


FIGURE 6 Energy minimized structure of hetero-coupled coordination molecular biscapsule **11** by Hyperchem 7.5® (MM + force field; the heptyl feet groups have been substituted by methyl groups for clarity).

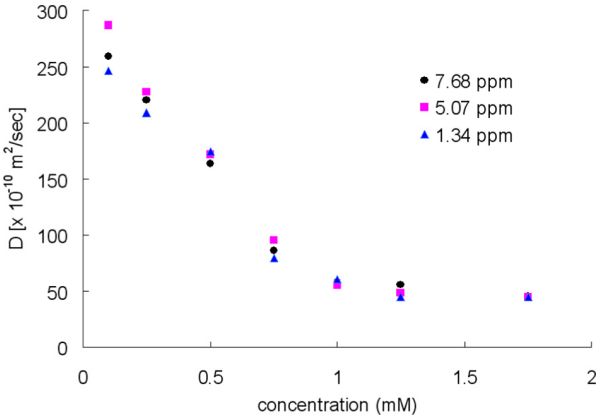


FIGURE 7 The concentration dependence of diffusion coefficients ($\times 10^{-10}$) of octacyanobiscavitand **4**-Pd(dppp)OTf_2 in $CDCl_3$ at 298 K.

EXPERIMENTS

Synthesis of Octabromobiscavitand 8

A mixture of hexadecol **6** (1.9 g, 1.1 mmol), NBS (4.6 g, 25.8 mmol) and MEK (100 mL) was stirred at 25°C overnight and then concentrated to 40 mL. Acetonitrile (100 mL) was added and the mixture was concentrated to 40 mL, cooled to RT, and then filtered. The filtered precipitate (~2.09 g) was dissolved in a minimum amount of acetone, acetonitrile (50 mL) was added, and the mixture was concentrated to 30 mL. The precipitate was filtered and dried under high vacuum to give octabromohexadecol (1.5 g, 57%). Octabromohexadecol (500 mg, 0.21 mmol), $BrCH_2Cl$ (551 mg, 4.26 mmol) and K_2CO_3 (589 mg, 4.26 mmol) in 30 mL of dry DMF was stirred at 60°C under argon gas for 1 day. After cooling to room temperature, excess of K_2CO_3 was removed by filtering with a glass filter. The filtrate was washed with H_2O and brine, and extracted with CH_2Cl_2, dried over $MgSO_4$. After concentration of solvents, the residue was purified by silica gel column chromatography eluted with Hexane:CH_2Cl_2 (1:1) and the concentrate of the best portions was poured into *n*-hexane to give

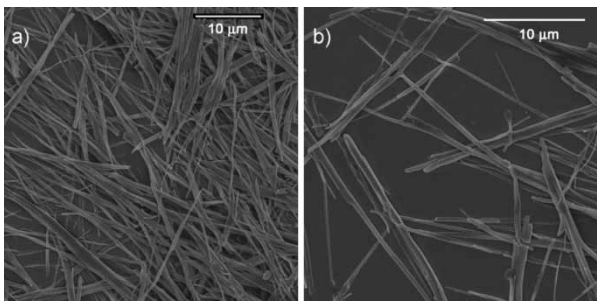


FIGURE 8 SEM images of **10**. a) 0.5 mM, b) 0.1 mM in $CHCl_3$, scale bar = 10 μm.

pure octabromobiscavitand **8** as a white solid (324 mg, 62%): m.p. >320°C (dec). MALDI-TOF MS calcd for m/z 2443.5, found 2442.9 (M^+100%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 25°C): δ = 7.72 (d, 4H, J = 8.4 Hz, biphenyl), 7.67 (d, 4H, J = 8.0 Hz, biphenyl), 7.18 (s, 4H, ArH), 6.93 (s, 4H, ArH), 6.56 (s, 2H, methine), 6.05–5.95 (m, 8H, outer OCHO), 4.86 (m, 6H, methine), 4.37–4.53 (m, 8H, inner OCHO), 2.01 (m, 12H, $CH_2(CH_2)_5CH_3$), 1.40–1.23 (m, 60H, $CH_2(CH_2)_5CH_3$), 0.87 (m, 18H, J = 4.0 Hz, $CH_2(CH_2)_5CH_3$); Anal. Calcd for $C_{118}H_{130}Br_8O_{16}$: C, 58.00; H, 5.36; Br, 26.16. Found: C, 58.03; H, 5.32, Br, 26.04.

Synthesis of Octacyanobiscavitand 4

To 4-cyanobenzenebronic acid (60 mg, 0.4 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.04 mmol) under an argon atmosphere were added argon-saturated THF (30 ml), argon-saturated EtOH (5 ml), and argon-saturated aqueous 2M KF (20 ml), and tetrabromocavitand **8** (100 mg, 0.04 mmol). The mixture was stirred at refluxing temperature for 4 days. After cooling to room temperature and evaporation of solvents, the residue was dissolved with CH_2Cl_2. The organic layer was washed with H_2O, and dried over $MgSO_4$. After concentration, the residue was purified by silica gel column chromatography eluted with Hexane:EtOAc:CH_3CN (15:15:3) and the concentrate of the best portions was poured into Hexane to give pure **4** as a white solid (60 mg, 56%): m.p. >320°C (dec). MALDI-TOF MS calcd for m/z 2621.2, found 2621.8 (M^+100%); ^{1}H NMR (400.1 MHz, $CDCl_3$, 50°C): δ = 7.82 (d, 4H, J = 8.4 Hz, feet-biphenyl), 7.68–7.59 (m, 20H, benzonitrile + feet-biphenyl), 7.52 (s, 4H, ArH), 7.27 (s, 4H, ArH), 7.22 (d, 8H, J = 8.0 Hz, benzonitrile), 7.14 (d, 8H, J = 8.0 Hz, benzonitrile), 6.55 (s, 2H, methine), 5.31–5.22 (m, 8H, outer OCHO), 4.86 (m, 6H, methine), 4.28 (d, 2H, J = 6.8 Hz, inner OCHO), 4.25 (d, 4H, J = 6.8 Hz, inner OCHO), 4.15 (d, 2H, J = 6.8 Hz, inner OCHO), 2.24 (m, 12H, $CH_2(CH_2)_5CH_3$), 1.49–1.26 (m, 60H, $CH_2(CH_2)_5CH_3$), 0.94–0.85 (m, 18H, $CH_2(CH_2)_5CH_3$); IR (KBr): 2226 cm^{-1} (CN); Anal. Calcd for $C_{174}H_{162}N_8O_{16}\cdot 4H_2O$: C, 77.60; H, 6.36; N, 4.16. found: C, 77.23; H, 6.36; N, 3.90.

Synthesis of Tetrakis(4-pyridyl)cavitand 9

To pyridine-4-bronic acid (410 mg, 2.0 mmol) and $Pd(PPh_3)_4$ (500 mg, 0.43 mmol) under an argon atmosphere were added argon-saturated THF (30 ml), argon-saturated EtOH (10 ml), and argon-saturated aqueous 2M KF (20 ml), and tetrabromocavitand **7** (500 mg, 0.40 mmol). The mixture was stirred at refluxing temperature for 4 days. After cooling to room temperature and evaporation of solvents, the residue was dissolved with CH_2Cl_2. The organic layer was washed with H_2O, and dried over $MgSO_4$. After concentration, the residue was purified by silica gel column chromatography eluted with MeOH:CH_2Cl_2 (1:4) and the concentrate of the best portions was poured into Hexane to give pure **9** as a white solid (286 mg, 58%): m.p. > 310°C (dec). FAB + MS calcd for m/z 1237.6, found 1237.6 (M^+100%). elemental analysis calcd for $C_{80}H_{92}N_4O_8\cdot 4H_2O$: C, 73.37; H, 7.70; N, 4.28. found: C, 73.50; H, 7.31; N, 4.61. ^{1}H NMR (400.1 MHz, $CDCl_3$, 25 °C): δ = 8.57 (d, 8H, J = 4.0 Hz, α-pyridyl), 7.36 (s, 4H, ArH), 6.97 (d, 8H, J = 4.0 Hz, β-pyridyl), 5.27 (d, 4H, J = 4.0 Hz, outer OCHO), 4.84 (t, 4H, J = 8.0 Hz, methine), 4.22 (d, 4H, J = 8.0 Hz, inner OCHO), 2.35 (m, 8H, $CH_2(CH_2)_5CH_3$), 1.50–1.33 (m, 40H, $CH_2(CH_2)_5CH_3$), 0.92 (t, 12H, J = 4.0 Hz, $CH_2(CH_2)_5CH_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 152.2, 149.5, 142.2, 138.6, 127.0, 125.0, 120.9, 100.4, 37.0, 31.9, 30.3, 29.8, 29.4, 27.9, 22.7, 14.1.

Homo-assembled Coordination Oligomeric Capsule 10

^{1}H NMR (400.1 MHz, CD_2Cl_2, 25°C) δ 6.45 (s, 2H, methine), 5.09–5.00 (br-m, 8H, outer OCHO), 4.77–4.71 (br-m, 6H, methine), 4.32–4.22 (br-m, 8H, inner OCHO), 2.85 (br-s, 16H, P—CH_2), 2.33–2.22 (br-m, 20H, $CH_2(CH_2)_5$CH3 + P—CH_2CH_2), 1.35–1.26 (m, 60H, $CH_2(CH_2)_5CH_3$), 0.92–0.85 (m, 18H, $CH_2(CH_2)_5CH_3$); IR (KBr): 2264 cm^{-1} (CN).

Hetero-assembled Coordination Molecular Biscapsule 11

^{1}H NMR (400.1 MHz, CD_2Cl_2, 25°C) δ 8.85 (s, 16H, α to N of pyridyl), 6.42 (s, 2H, methine), 5.61 (br-s, 8H, outer OCHO of pyridyl cavitand), 4.88–4.68 (br-m, 24H, outer OCHO and methine of octa-CN cavitand + methine of pyridyl cavitand), 4.31–4.23 (br-m, 16H, inner OCHO of octa-CN and pyridyl cavitand), 3.24 (br-s, 16H, CH_2—P—Pd—pyridyl), 2.90–2.78 (br-m, 32H, CH_2CH_2—P—Pd—CN) 2.37–2.21 (br-m, 28H, $CH_2(CH_2)_5$CH3), 1.35–1.26 (m, 140H, $CH_2(CH_2)_5CH_3$), 0.92–0.85 (m, 42H, $CH_2(CH_2)_5CH_3$); IR (KBr): 2229 cm^{-1} (CN).

The Pulse-field Gradient Spin-echo (PGSE) NMR Experiment [36–39]

NMR diffusion measurements were performed on a Bruker Avance 600 MHz spectrometer equipped with a microprocessor-controlled gradient unit and ultra-stable temperature control unit. The experiments were conducted in a 5 mm TXI cryoprobe at 298 K. The diffusion experiments were performed using the biopolar pulse longitudinal encode-decode (BPLED). Diffusion gradient length was 2.2 ms and the diffusion time was 50–100 ms. The amplitudes of gradient pulses ranged from 1 G/m to 40 G/m. Diffusion coefficients were calculated from the data

obtained by 2D diffusion-ordered spectroscopy (DOSY).

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