

Dynamic Equilibrium between a Supramolecular Capsule and Bowl Generated by Inter- and Intramolecular Metal Clipping

Seong Jin Park,^[a] Dong Mok Shin,^[a] Shigeru Sakamoto,^[b] Kentaro Yamaguchi,^[b] Young Keun Chung,^[a] Myoung Soo Lah,^[c] and Jong-In Hong*^[a, d]

Abstract: The metal-induced self-assembly of a resorcin[4]arene derivative **1** that has four pyridine units as pendent groups and two equivalents of $[M(dppp)(OTf)_2]$ ($M = Pd, Pt$) results in a dynamic equilibrium between an interclipped supramolecular capsule **3** and an intraclipped bowl **4** in nitromethane, although the interclipped capsule **3** is formed as a sole adduct in chloroform/methanol and the intraclipped bowl **4** is formed exclusively in an aqueous phase. This demonstrates how metal-induced self-assembly can be tuned by subtle changes in the solvent system. The coexistence of the two

structures in nitromethane was characterized by NMR spectroscopy and coldspray ionization mass spectrometry (CSI-MS). The crystal structure of the interclipped capsule **3b**, which is composed of two units of ligand **1** and four Pt^{II} ions, reveals the capsule cavity to have nanoscale dimensions of $15 \times 20 \text{ \AA}$. NMR spectra show that the dynamic equilibrium between **3** and **4** is

Keywords: dynamic equilibrium · interclipped capsule · intraclipped bowl · self-assembly · solvent effects

dependent on concentration and temperature. Temperature-dependent 1H NMR spectroscopy was carried out from 273 to 343 K to verify the thermodynamic parameters that control the dynamic equilibrium process; the conversion from the interclipped supramolecular capsule **3a** to the intraclipped bowl **4a** is entropically favored and enthalpically disfavored. The rotational barrier of the restricted rotation of pyridine units in the intraclipped bowl **4** was determined by line-shape analysis.

[a] S. J. Park, D. M. Shin, Prof. Dr. Y. K. Chung, Prof. Dr. J.-I. Hong
School of Chemistry, College of Natural Sciences
Seoul National University
Seoul 151-747 (Korea)
Fax: (+82)2-889-1568
E-mail: jihong@plaza.snu.ac.kr

[b] Dr. S. Sakamoto, Prof. Dr. K. Yamaguchi
Chemical Analysis Center
Chiba University
Chiba 263-8522 (Japan)

[c] Prof. Dr. M. S. Lah
Department of Chemistry, College of Science
Hanyang University
Ansan, Kyunggi-Do 425-791 (Korea)

[d] Prof. Dr. J.-I. Hong
Center for Molecular Design and Synthesis
KAIST, Daejeon 305-701 (Korea)

Introduction

Metal-induced self-assembly is a flourishing area in the field of host-guest and supramolecular chemistry. There are many examples of the metal-mediated self-assembly of squares,^[1] helices,^[2] grids,^[3] catenanes,^[4] cylinders,^[5] circular helicates,^[6] and cages.^[7] It appears from these studies that a self-assembled structure can be predicted if the metal and ligand are chosen correctly. Many superstructures have been designed in this manner; however, there are a growing number of examples that deviate from the structures expected. Dynamically assembled structures, such as molecular triangles/squares,^[8] dimeric/trimeric (or tetrameric) assemblies,^[9] tetrameric/hexameric circular complexes,^[10] grid/helical architectures,^[11] and coordination boxes^[12] have also been reported.

We have extensively investigated the formation of superstructures composed of resorcin[4]arene derivatives (**1**) that have four pyridine (Py) units as pendent groups and *cis*-protected square-planar M^{II} ions ($M = Pd, Pt$). We recently reported that, following the mixing of ligand **1** with two equivalents of organic- and water-soluble Pd^{II} or Pt^{II} ions, respec-

Supporting information for this article is available on the WWW under <http://www.chemurj.org/> or from the author: Characterization of the resorcin[4]arene-based ligand **1**. Experimental data (1H NMR monitoring, $^1H, ^1H$ -COSY, and CSI-MS spectrum) of the exclusive formation of **3** in a chloroform/methanol solution. Experimental data (CSI-MS, $^1H, ^1H$ -COSY, ^{31}P NMR, ^{19}F NMR, CSI-MS spectra, and 1H NMR monitoring) of the dynamic equilibrium between **3** and **4** in nitromethane. Van't Hoff plot of the dynamic equilibrium between **3a** and **4a**

tively, the interclipped nanoscale capsule (composed of two units of ligand **1** and four metal ions) was constructed as a sole adduct in chloroform/methanol, whereas the intracapped bowl (composed of one ligand **1** and two metal ions), was exclusively formed in an aqueous phase (Scheme 1a).^[7e,13] Here we describe the dynamic equilibrium between an interclipped capsule **3** and an intracapped bowl **4** in nitromethane (Scheme 1b). We demonstrate that the metal-mediated, self-assembled superstructures can be tuned by subtle changes in the solvent system. This is the first example of the formation and dynamic equilibrium of a three-dimensional supramolecular system, in which the intra- and interclipped structures are formed from three-dimensional ligands in a dynamic manner.

Results and Discussion

Dynamic equilibrium between an interclipped capsule (3) and an intracapped bowl (4): A resorcin[4]arene-based ligand **1** with four pyridine substituents at the upper rim was prepared from the corresponding tetrol cavitand^[14] and 4-picolyl chloride by nucleophilic substitution.^[7e] Following the simple addition of two equivalents of $[M(\text{dppp})(\text{OTf})_2]$ ($M = \text{Pd}, \text{Pt}$) to resorcin[4]arene derivative **1** in $[\text{D}_3]$ nitromethane, two sets of ^1H NMR peaks were visible (see Supporting Information).^[15] One set of these signals showed the same pattern as that observed in $[\text{D}]$ chloroform/ $[\text{D}_4]$ methanol, in which the D_{4h} -symmetric capsule was predominant.^[7e] The other structure had C_{2v} symmetry, as seen from extensive one-dimensional and two-dimensional ^1H NMR spectroscopy measurements. Due to the D_{4h} symmetry of **3**, each

bridging methylene proton (H_i, H_o) leads to a single doublet signal.^[7e] The signals for the C_{2v} -symmetric structure **4**, however, are split into two sets of signals.^[13] Since H_i and H_o reside in the shielding region between the two pyridine ligands that interact with the metal ions, it is expected that they will move further upfield than H_i and H_o . Upon intracapping with Pd^{II} ions, the pyridyl protons (H_p), as well as the α - and β -protons ($\text{H}_\alpha, \text{H}_\beta$) of the pyridine units, become desymmetrized by the hindered rotation upon Pd^{II} complexation, and appear as a pair of doublets. In addition, the methine and methyl protons ($\text{H}_b/\text{H}_{b'}$, $\text{H}_c/\text{H}_{c'}$) of the lower rim become desymmetrized and appear as a pair of doublets or as a multiplet.

Additional evidence for the coexistence of two distinct supramolecular species was obtained from the ^{31}P NMR spectrum (see Supporting Information). This exhibited two discrete peaks at around 9.27 and 9.22 ppm, indicating that two kinds of phosphorus atoms exist in two different environments.^[16]

The coldspray ionization mass spectrometric (CSI-MS) measurement (Figure 1) clearly shows the coexistence of an interclipped capsule **3a** and an intracapped bowl **4a** in nitro-

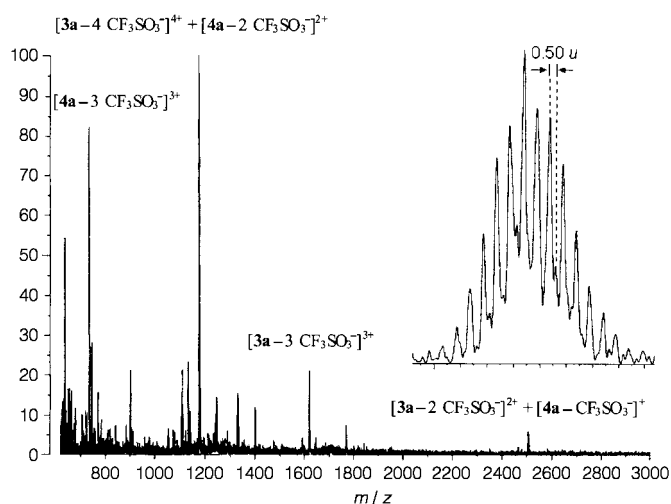
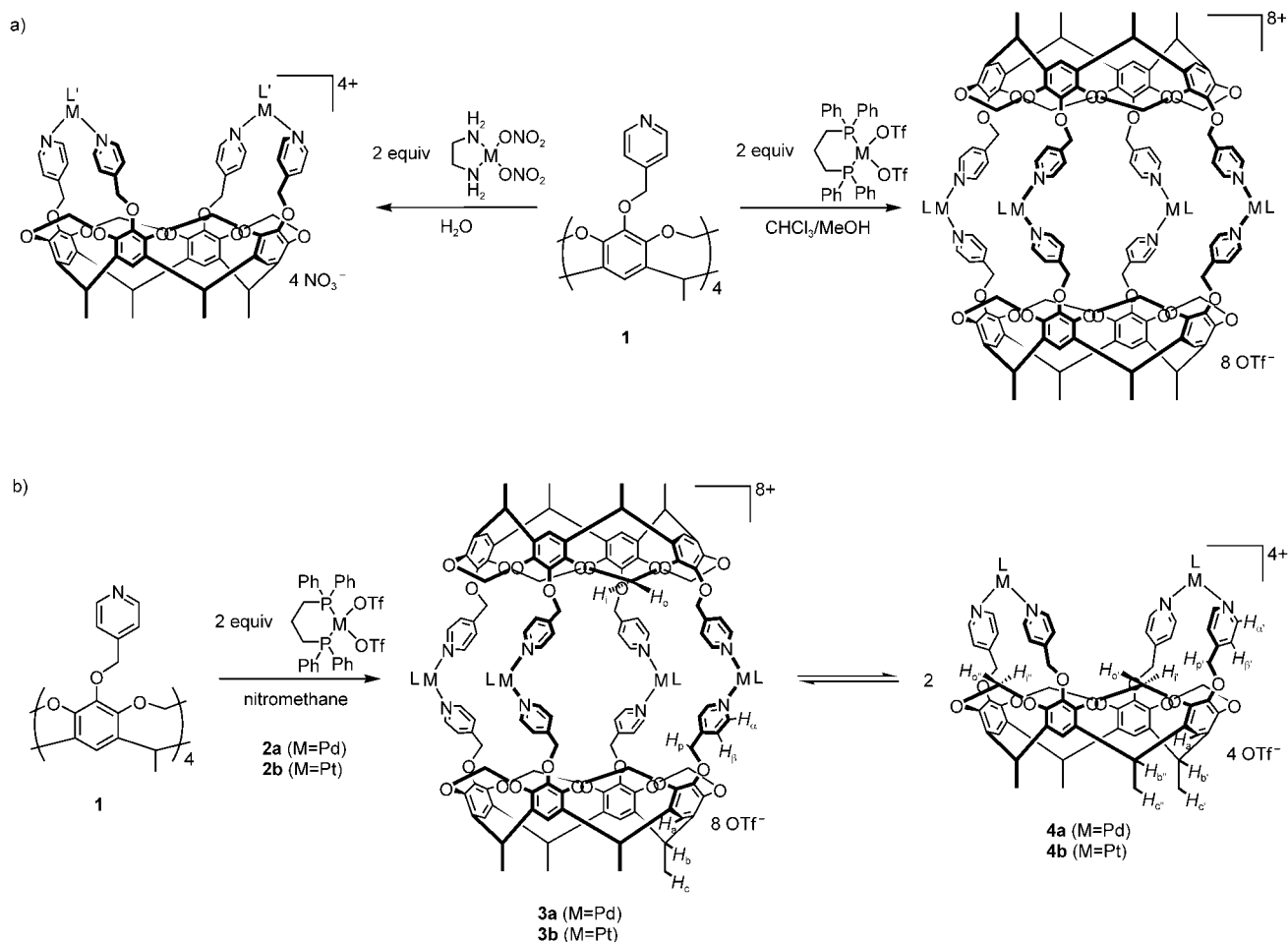


Figure 1. CSI-MS spectrum of **1** and **2a** in a 1:2 molar ratio in nitromethane (needle voltage: 2.0 kV, needle current: 300–700 nA, orifice voltage: 0 V, ringlens voltage: 300 V, ion source temperature: 293 K, flow rate: $8\mu\text{L}\cdot\text{min}^{-1}$). The inset shows the superimposition of signals from the singly charged species $[\mathbf{4a}-\text{CF}_3\text{SO}_3]^{-}$ and the doubly charged species $[\mathbf{3a}-2\text{CF}_3\text{SO}_3]^{2+}$.

methane containing **1** and **2a** in a 1:2 molar ratio: $[\mathbf{3a}-2\text{CF}_3\text{SO}_3]^{2+}$ (m/z : 2506.2), $[\mathbf{3a}-3\text{CF}_3\text{SO}_3]^{3+}$ (m/z : 1621.3), $[\mathbf{3a}-4\text{CF}_3\text{SO}_3]^{4+}$ (m/z : 1178.2), $[\mathbf{4a}-\text{CF}_3\text{SO}_3]^{-}$ (m/z : 2506.2), $[\mathbf{4a}-2\text{CF}_3\text{SO}_3]^{2+}$ (m/z : 1178.2), and $[\mathbf{4a}-3\text{CF}_3\text{SO}_3]^{3+}$ (m/z : 735.9). Because the mass of **3** is exactly twice the mass of **4**, the signals attributed to the doubly and quadruply charged species of **3** are superimposed by the singly and doubly charged signals of **4** with different m/z ratios. The inset in Figure 1 shows the overlap-

Abstract in Korean:

레스신[4]아렌을 골격으로 갖는 피리딘 리간드와 2 당량의 팔라듐(II) 이온 또는 백금(II) 이온이 자기조립하게 될 때, 클로로포름-메탄올 혼합 용매에서는 두 개의 리간드 분자 사이에 묶인 분자캡슐이 만들어지고 수용액에서는 한 개의 리간드 분자 내에서 묶인 분자사발이 형성되지만 니트로메탄 용액에서는 분자 사이에 묶인 분자캡슐과 분자 내에서 묶인 분자사발 사이에 동적 평형이 존재함을 알 수 있었다. 이것을 통해서 금속이온-리간드 자기조립 현상이 용매 시스템의 미세한 변화에 의해서 조절될 수 있음을 알 수 있다. 니트로메탄 용액에서 두 가지 초분자가 함께 존재하고 있음을 핵자기공명분광법과 질량분석법을 통해서 밝혔다. 분자 사이에 묶인 분자캡슐의 구조는 X 선 결정구조를 통하여 명확히 밝혔다. 분자캡슐의 내부 공간은 15 Å X 20 Å 의 나노 크기를 가짐을 알 수 있었다. 핵자기공명분광법을 통해서 분자사발과 분자캡슐 사이의 동적 평형이 농도와 온도에 의존함을 알 수 있었다. 절대온도 273 도와 343 도 사이에서 온도를 변화시키면서 핵자기공명 현상을 조사함으로써 동적 평형의 열역학적 상수를 구할 수 있게 되었다. 이로부터 분자캡슐에서 분자사발로 변화하는 현상은 엔탈피상으로는 유리하고 엔탈피상으로는 불리함을 알 수 있었다. 분자사발의 피리딘 부분이 자유롭게 회전하지 못하는 현상을 온도변화에 따른 핵자기공명 현상을 통해 알 수 있었는데 회전장벽 에너지 값은 핵자기공명분광법을 통해서 구할 수 있었다.



Scheme 1. Metal-induced self-assembly of a resorcin[4]arene derivative **1** and two equivalents of M^{II} ions (**2**): a) exclusive formation of an intra or interclipped superstructure; b) dynamic equilibrium between an interclipped capsule **3** and an intracapped bowl **4**. $M = Pd$ or Pt , $L = 1,3$ -bis(diphenylphosphino)propane (dppp), $L' =$ ethylenediamine (en), $OTf = OSO_2CF_3$.

ping of signals arising from a singly charged **4a** and a doubly charged **3a**.

The structure of the interclipped capsule **3b** was corroborated by means of X-ray crystallography (Figure 2).^[17] A single crystal that was suitable for X-ray structural analysis was obtained by the slow diffusion, at ambient temperature for five days, of ethanol into a chloroform/methanol mixture that contained a minute quantity of *p*-xylene.^[18] The crystal structure of **3b** clearly demonstrated that the two resorcin[4]arene-based pyridine ligands were clipped by four Pt^{II} ions. The adjacent $Pt \cdots Pt$ distances are 10.9 and 17.1 Å, and the distances between the two remote Pt atoms are 20.1 and 20.5 Å. The distance between the centroids of the four resorcin[4]arene methine carbon atoms on the bottom rim is approximately 15.4 Å. Therefore, the cavity of **3b** has nanoscale dimensions of 15×20 Å, and could encapsulate positively charged *N*-alkyl pyridinium derivatives due to strong cation- π interactions.^[7e] The $N_{Py} \cdots Pt \cdots N_{Py}$ angles of 85.1° and 86.5° are considerably smaller than the ideal square-planar angles of 90°. This is presumably due to the need for larger $P_{dppp} \cdots Pt \cdots P_{dppp}$ angles (91.2 to 94.7°) for the chelating dppp

unit.^[1j] One interesting feature of the complex is that one of the dppp phenyl groups is positioned almost parallel with and on top of the chelated pyridine unit.^[1j]

Concentration- and temperature-dependent 1H NMR studies of the dynamic equilibrium between an interclipped capsule (3**) and an intracapped bowl (**4**):** To elucidate the behavior of the dynamic equilibrium between the interclipped capsule **3** and the intracapped bowl **4**, concentration-dependent 1H NMR spectroscopy was performed on a 1:2 molar mixture of **1** and **2a**. Figure 3 shows how reduction of the concentration results in an increase in the height of the peaks that are assigned to bowl **4a**; the relative ratios of **4a/3a** are 1.64, 2.66, and 4.26 at 4.0, 2.0, and 1.0 mM of **1**, respectively. This indicates that the major component at lower concentrations is the intracapped bowl **4**, which is assembled from fewer components than capsule **3**.

To verify the thermodynamic parameters that control this dynamic equilibrium, temperature-dependent 1H NMR spectroscopy was carried out from 273 to 343 K (Table 1). As the temperature increases, the integral of the peaks that are assigned to bowl **4** increases; the relative ratios of **4a/3a** are

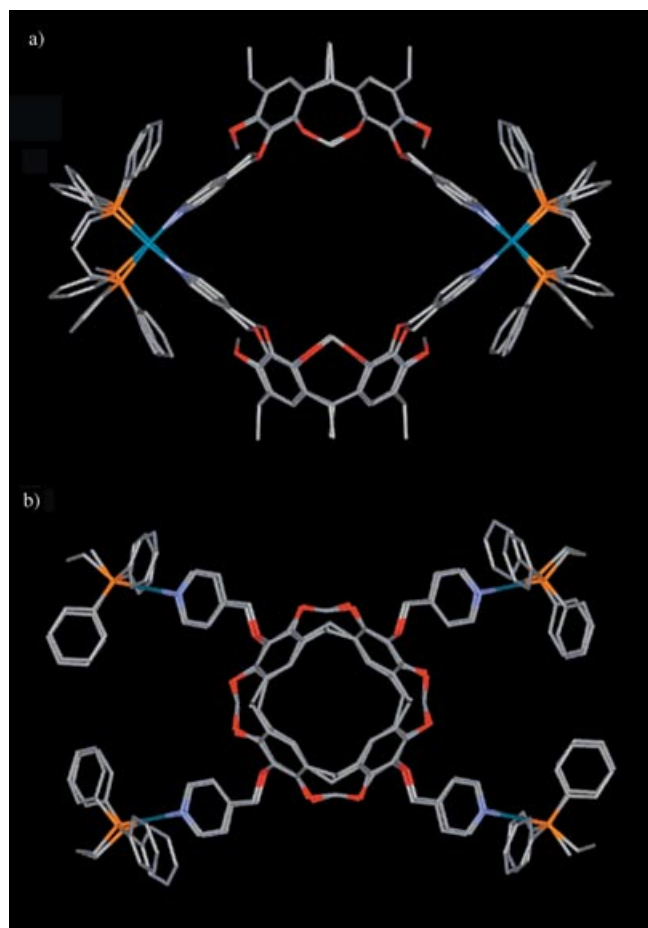


Figure 2. The X-ray crystal structure of **3b**: a) side view; b) top view. For clarity, the triflate anions and solvent molecules have been omitted.

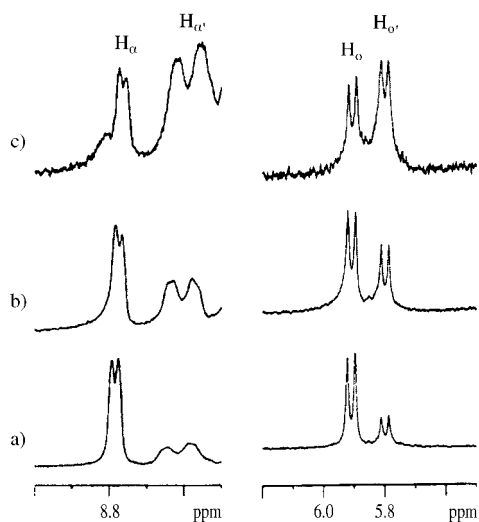


Figure 3. Concentration-dependent ^1H NMR spectra showing the dynamic equilibrium between capsule **3a** and bowl **4a** (300 MHz, $[\text{D}_3]$ nitro-methane, 298 K): a) $[\mathbf{1}]_0 = 4 \text{ mM}$; b) $[\mathbf{1}]_0 = 2 \text{ mM}$; c) $[\mathbf{1}]_0 = 1 \text{ mM}$.

2.0, 2.7, 5.7, and 9.5 at 273, 293, 313, and 343 K, respectively.^[19,20] The thermodynamic equilibrium constant K_{eq} for the equilibrium between **3** and **4** can be calculated from Equa-

Table 1. Temperature-dependent equilibrium constant K_{eq} in $[\text{D}_3]$ nitro-methane ($[\mathbf{1}]_0 = 1.3 \text{ mM}$). The equilibrium constants were calculated from the integration of well-separated H_α and H_β signals).

Temperature [K]	[3a] [M]	[4a] [M]	K_{eq} [M]	$\ln K_{\text{eq}}$
273	3.27×10^{-4}	6.47×10^{-4}	1.28×10^{-3}	-6.66
283	2.86×10^{-4}	7.28×10^{-4}	1.86×10^{-3}	-6.29
293	2.79×10^{-4}	7.42×10^{-4}	1.97×10^{-3}	-6.23
298	2.40×10^{-4}	8.21×10^{-4}	2.81×10^{-3}	-5.87
304	2.16×10^{-4}	8.67×10^{-4}	3.47×10^{-3}	-5.66
305	2.10×10^{-4}	8.79×10^{-4}	3.68×10^{-3}	-5.61
306	2.04×10^{-4}	8.93×10^{-4}	3.91×10^{-3}	-5.54
307	1.98×10^{-4}	9.04×10^{-4}	4.12×10^{-3}	-5.49
308	2.04×10^{-4}	8.92×10^{-4}	3.90×10^{-3}	-5.55
309	1.95×10^{-4}	9.09×10^{-4}	4.23×10^{-3}	-5.46
310	1.86×10^{-4}	9.27×10^{-4}	4.62×10^{-3}	-5.38
313	1.68×10^{-4}	9.64×10^{-4}	5.53×10^{-3}	-5.20
323	1.44×10^{-4}	1.01×10^{-3}	7.14×10^{-3}	-4.94
333	1.20×10^{-4}	1.06×10^{-3}	9.37×10^{-3}	-4.67
343	1.13×10^{-4}	1.07×10^{-3}	1.02×10^{-2}	-4.59

tion (1), and the concentration of the two species, **[3]** and **[4]**, can be calculated from the integration of H_α proton (I_{H_α}) and H_β proton (I_{H_β}), by using Equations (2) and (3).

$$K_{\text{eq}} = [\mathbf{4}]^2 / [\mathbf{3}] \quad (1)$$

$$[\mathbf{3}] = 0.5 [\mathbf{1}]_0 \{I_{\text{H}_\alpha} / (I_{\text{H}_\alpha} + 2 I_{\text{H}_\beta})\} \quad (2)$$

$$[\mathbf{4}] = [\mathbf{1}]_0 \{2 I_{\text{H}_\beta} / (I_{\text{H}_\alpha} + 2 I_{\text{H}_\beta})\} \quad (3)$$

In Equations (2) and (3), $[\mathbf{1}]_0 = 2[\mathbf{3}] + [\mathbf{4}]$ ($[\mathbf{1}]_0$: initial concentration of ligand **1**) and $[\mathbf{3}]:[\mathbf{4}] = I_{\text{H}_\alpha}:4 I_{\text{H}_\beta}$.

Enthalpy and entropy values of the supramolecular equilibrium were obtained by using the van't Hoff equation: $H^\circ = 25.2 \text{ kJ mol}^{-1}$ and $S^\circ = 36.1 \text{ J K}^{-1} \text{ mol}^{-1}$. These values show that the conversion from **3a** to **4a** is enthalpically disfavored, but entropically favored. Presumably the high enthalpic cost is attributable to the difficulty in forming the intracapped structure, which possesses a short tether unit that connects four pyridine units from the resorcin[4]arene backbone. The favorable entropy is due to the formation of two equivalents of **4** from one equivalent of **3**, and/or from the release of encapsulated solvent molecules into the bulk, following the collapse of the interclipped supramolecular capsule **3** to form the intracapped bowl **4**.

Restricted rotation of pyridine units in an intracapped bowl (4): The restricted rotation of the pyridine units in the intracapped bowl **4a** was also observed by performing temperature-dependent ^1H NMR spectroscopy (Figure 4). The rotational barrier was determined by line-shape analysis with regard to the signals associated with the pyridine units.

The α - and β -protons (H_α , H_β) of the pyridine units in the intracapped bowl **4** displayed two sets of well-separated doublet peaks at ambient temperature, whereas protons H_α and H_β in the interclipped capsule **3** showed only one set of doublet peaks. These two sets of signals for the pyridine units in **4** coalesced to a single set at 306 K.

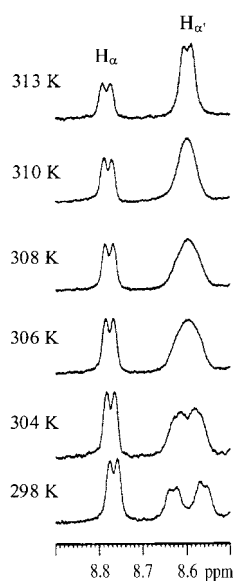


Figure 4. Section of the ^1H NMR spectra, recorded at various temperatures (300 MHz, $[\text{D}_3]$ nitromethane, $[\mathbf{1}]_0 = 1.3 \text{ mM}$).

The free energy of activation ΔG^\ddagger (in J mol^{-1}) can be determined by using the Eyring equation [Eq. (4)], in which x (transmission coefficient) is usually assumed to have a value of 1, together with Equation (5),^[21] in which T_c is the coalescence temperature and k_c is the rate constant at T_c .

$$k = x \frac{k_B T}{h} e^{-\Delta G^\ddagger / RT} \quad (4)$$

$$\Delta G_c^\ddagger = 19.14 T_c \left(10.32 + \log \frac{T_c}{k_c} \right) \quad (5)$$

In Equation (5), $k_c = 2.2 \Delta\nu$ ($\Delta\nu$: separation in Hz between the two signals in the absence of exchange).

In this system, T_c and $\Delta\nu$ were determined from ^1H NMR spectra to be 306 K and 66.8 Hz, respectively. The free energy of activation ΔG^\ddagger for rotation of the pyridine units in the intracapped bowl $\mathbf{4a}$ was calculated to be 62.3 kJ mol^{-1} .

Presumably, the origin of this phenomenon is the increasing rotational freedom of the intracapped $\text{N}_{\text{Py}}\text{-Pd-N}_{\text{Py}}$ bonds, and/or the acceleration of the association–dissociation rate of the $\text{N}_{\text{Py}}\text{-Pd}$ bond at elevated temperature.

Conclusion

We have shown that metal-induced self-assembly can be tuned by subtle changes in the solvent system; dynamic equilibrium between an interclipped supramolecular capsule $\mathbf{3}$ and an intracapped bowl $\mathbf{4}$ exists when a resorcin[4]arene derivative $\mathbf{1}$ and $[\text{M}(\text{dppp})(\text{OTf})_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) are mixed in a 1:2 molar ratio in nitromethane, although the interclipped capsule $\mathbf{3}$ is formed as a sole adduct in chloroform/methanol

and the intracapped bowl $\mathbf{4}$ is formed exclusively in an aqueous phase. This indicates that self-assembly can be controlled by changing the nature of the surrounding solvent medium. NMR studies confirm that the dynamic equilibrium between $\mathbf{3}$ and $\mathbf{4}$ is dependent on concentration and temperature. The thermodynamic parameters that control the dynamic equilibrium were elucidated; the conversion from $\mathbf{3a}$ to $\mathbf{4a}$ is entropically favored and enthalpically disfavored. The restricted rotation of pyridine units in the intracapped bowl $\mathbf{4}$ was also observed, and the rotational barrier was determined by line-shape analysis.

Experimental Section

General: All of the chemicals were of reagent grade and were used without further purification. Deuterated solvents were acquired from Cambridge Isotopic Laboratories and were used for the complexation reactions and for NMR spectrometric measurements. All NMR spectra were recorded on either a Bruker Avance DPX-300 or a Bruker Avance 500 spectrometer. ^1H NMR spectra were recorded at 300 and 500 MHz, and the chemical shifts were reported in ppm, with the residual resonance of deuterated solvent as an internal reference ($\delta = 7.27 \text{ ppm}$ for $[\text{D}]\text{chloroform}$; $\delta = 4.33 \text{ ppm}$ for $[\text{D}_3]\text{nitromethane}$). ^{13}C NMR spectra were recorded at 75 MHz, and the chemical shifts were given in ppm relative to the carbon resonance of deuterated solvent ($\delta = 77.0 \text{ ppm}$ for $[\text{D}]\text{chloroform}$). ^{19}F NMR spectra were recorded at 282 MHz, and the chemical shifts were reported relative to external standards of CFCl_3 at 0.00 ppm. ^{31}P NMR spectra were recorded at 202 MHz, and the chemical shifts were given relative to external standards of H_3PO_4 at 0.00 ppm. Fast atom bombardment mass spectrometry (FAB-MS) data were obtained by using a JEOL JMS-AX505WA mass spectrometer with *m*-nitrobenzyl alcohol (NBA) as a matrix. CSI-MS data were measured on a four-sector (BE/BE) tandem mass spectrometer (JEOL JMS-700T) equipped with a CSI source. Data for the crystal structure of the interclipped supramolecular capsule $\mathbf{3b}$ were recorded by using an Enraf-Nonius Kappa-CCD diffractometer equipped with a graphite crystal incident-beam monochromator *Lp*.

Synthesis of resorcin[4]arene-based ligand (1): A mixture of corresponding tetrol cavitant (132 mg, 0.2 mmol),^[14] K_2CO_3 (690 mg, 5.0 mmol), and 4-picolyl chloride hydrochloride (328 mg, 2.0 mmol) in dry DMF (5 mL) was stirred under a nitrogen atmosphere at 60°C for 18 h. The solvent was evaporated under vacuum and the residue was dissolved in chloroform (50 mL). The solution was washed with water and brine, then dried (MgSO_4), and evaporated to dryness under vacuum. Silica gel chromatography with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (10:1) was used to obtain $\mathbf{1}$ (yield 165 mg; 80%). ^1H NMR (300 MHz, $[\text{D}]\text{chloroform}$): $\delta = 8.61$ (d, $^3J(\text{H,H}) = 5.85 \text{ Hz}$, 8H; PyH_α), 7.33 (d, $^3J(\text{H,H}) = 5.71 \text{ Hz}$, 8H; PyH_β), 7.02 (s, 4H; ArH), 5.81 (d, $^2J(\text{H,H}) = 7.12 \text{ Hz}$, 4H; $\text{ArOCH}_2\text{H}_2\text{OAr}$), 5.1–4.9 (m, 12H; $\text{CHCH}_3 + \text{OCH}_2\text{Py}$), 4.50 (d, $^2J(\text{H,H}) = 7.13 \text{ Hz}$, 4H; $\text{ArOCH}_2\text{H}_2\text{OAr}$), 1.78 ppm (t, $^3J(\text{H,H}) = 7.42 \text{ Hz}$, 12H; CHCH_3); ^{13}C NMR (75 MHz, $[\text{D}]\text{chloroform}$): $\delta = 149.56, 147.66, 147.15, 143.97, 139.99, 121.54, 114.18, 99.45, 73.40, 31.23, 15.82 \text{ ppm}$; FAB-MS: m/z : 1021.3663 $[\text{M}+\text{H}]^+$ (calcd: 1021.3660); elemental analysis (%) calcd for $\text{C}_{60}\text{H}_{52}\text{N}_4\text{O}_{12} \cdot \text{CH}_2\text{Cl}_2$: C 66.24, H 4.92, N 5.07; found: C 65.33, H 5.17, N 4.97.

Synthesis of interclipped capsule (3a) and intracapped bowl (4a): Resorcin[4]arene-based ligand $\mathbf{1}$ (10.2 mg, 0.010 mmol) and $[\text{Pd}(\text{dppp})(\text{OTf})_2]$ (16.4 mg, 0.020 mmol) were mixed in CH_3NO_2 (3.0 mL) for a few minutes at ambient temperature, then the mixture was concentrated to 1.0 mL. Et_2O was added to the reaction mixture, and the resulting white precipitate was collected by filtration, washed with Et_2O , and dried under vacuum to give the product (yield 22.5 mg; 85%). ^1H NMR (300 MHz, $[\text{D}_3]\text{nitromethane}$): $\delta = 8.83$ (d, $^3J(\text{H,H}) = 5.43 \text{ Hz}$, 16H; H_α), 8.65 (br, 8H; H_α), 7.90 (br, 48H; $\text{P}(\text{C}_6\text{H}_2\text{H}_3)_2\text{CH}_2$), 7.57 (br, 72H; $\text{P}(\text{C}_6\text{H}_2\text{H}_3)_2\text{CH}_2$), 7.32 (br, 28H; $\text{H}_\beta + \text{H}_\alpha + \text{H}_\alpha$), 7.23 (br, 8H; H_β), 5.95

(d, $^2J(\text{H,H})=7.36$ Hz, 8H; H_o), 5.84 (d, $^2J(\text{H,H})=6.55$ Hz, 2H; H_o), 5.02 (d, $^2J(\text{H,H})=15.47$ Hz, 4H; H_p), 4.89 (br, 24H; H_p+H_b), 4.69 (d, $^2J(\text{H,H})=15.82$ Hz, 4H; H_p), 4.42 (m, 4H; H_b+H_v), 4.17 (d, $^2J(\text{H,H})=6.53$ Hz, 2H; H_i), 3.53 (br, 8H; PCH_2CH_2), 3.41 (br, 16H; PCH_2CH_2), 3.31 (br, 4H; PCH_2CH_2), 3.12 (d, $^2J(\text{H,H})=6.47$ Hz, 2H; H_o), 2.48 (br, 10H; $H_r+\text{PCH}_2\text{CH}_2$), 1.76 (t, $^3J(\text{H,H})=6.93$ Hz, 12H; H_c), 1.67 ppm (m, 12H; H_c+H_o); ^{19}F NMR (282 MHz, $[\text{D}_3]$ nitromethane): $\delta=-82.32$ ppm; ^{31}P NMR (202 MHz, $[\text{D}_3]$ nitromethane): $\delta=9.27, 9.22$ ppm; CSI-MS: m/z : 2506.2 $[\mathbf{3a}-2\text{CF}_3\text{SO}_3^-]^{2+}$, 1621.3 $[\mathbf{3a}-3\text{CF}_3\text{SO}_3^-]^{3+}$, 1178.2 $[\mathbf{3a}-4\text{CF}_3\text{SO}_3^-]^{4+}$, 2506.2 $[\mathbf{4a}-\text{CF}_3\text{SO}_3^-]^{2+}$, 1178.2 $[\mathbf{4a}-2\text{CF}_3\text{SO}_3^-]^{2+}$, 735.9 $[\mathbf{4a}-3\text{CF}_3\text{SO}_3^-]^{3+}$.

Acknowledgement

Financial support from the MOST (Grant No. M10213030002-03B1503-00210) is gratefully acknowledged. S.J.P. and D.M.S. thank the Ministry of Education for the award of BK 21 fellowships.

- [1] a) P. Angaridis, J. F. Berry, F. A. Cotton, C. A. Murillo, X. Wang, *J. Am. Chem. Soc.* **2003**, *125*, 10327–10334; b) S. J. Lee, W. Lin, *J. Am. Chem. Soc.* **2002**, *124*, 4554–4555; c) K.-B. Shiu, H.-C. Lee, G.-H. Lee, Y. Wang, *Organometallics* **2002**, *21*, 4013–4016; d) S.-S. Sun, A. Lees, *Eur. J. Inorg. Chem.* **2001**, *40*, 3154–3160; e) F. A. Cotton, C. Lin, C. A. Murillo, S.-Y. Yu, *J. Chem. Soc. Dalton Trans.* **2001**, 502–504; f) M. Aoyagi, K. Biradha, M. Fujita, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1369–1373; g) K.-S. Jeong, Y. L. Cho, J. U. Song, H.-Y. Chang, M.-G. Choi, *J. Am. Chem. Soc.* **1998**, *120*, 10982–10983; h) P. J. Stang, D. H. Cao, K. Chen, G. M. Gray, D. C. Muddiman, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 5163–5168; i) P. J. Stang, J. Fan, B. Olenyuk, *Chem. Commun.* **1997**, 1453–1454; j) P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 6273–6283.
- [2] a) J. Hamacek, S. Blanc, M. Elhabiri, E. Leize, A. Van Dorsselaer, C. Piguet, A.-M. Albrecht-Gary, *J. Am. Chem. Soc.* **2003**, *125*, 1541–1550; b) H.-J. Kim, D. Moon, M. S. Lah, J.-I. Hong, *Angew. Chem.* **2002**, *114*, 3306–3309; *Angew. Chem. Int. Ed.* **2002**, *41*, 3174–3177; c) B. Bocquet, G. Bernardinelli, N. Ouali, S. Floquet, F. Renaud, G. Hopfgartner, C. Piguet, *Chem. Commun.* **2002**, 930–931; d) N. Fatin-Rouge, S. Blanc, A. Pfeil, A. Rigault, A.-M. Albrecht-Gary, J.-M. Lehn, *Helv. Chim. Acta* **2001**, *84*, 1694–1711; e) J. Xu, T. N. Parac, K. N. Raymond, *Angew. Chem.* **1999**, *111*, 1690–1694; *Angew. Chem. Int. Ed.* **1999**, *38*, 2878–2882; f) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062.
- [3] a) D. M. Shin, I. S. Lee, Y. K. Chung, M. S. Lah, *Inorg. Chem.* **2003**, *42*, 5459–5461; b) E. Breuning, G. S. Hanan, F. J. Romero-Salguero, A. M. Garcia, P. N. W. Baxter, J.-M. Lehn, E. Wegelius, K. Rissanen, H. Nierengarten, A. van Dorsselaer, *Chem. Eur. J.* **2002**, *8*, 3458–3466; c) Y. Zhao, M. Hong, D. Sun, R. Cao, *J. Chem. Soc. Dalton Trans.* **2002**, 1354–1357; d) K. Biradha, M. Fujita, *Chem. Commun.* **2001**, 15–16; e) A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **1999**, *5*, 1803–1808; f) L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc.* **1998**, *120*, 2676–2677.
- [4] a) P. Mobian, J.-M. Kern, J.-P. Sauvage, *Inorg. Chem.* **2003**, *42*, 8633–8637; b) C. Dietrich-Buchecker, B. Colasson, M. Fujita, A. Hori, N. Geum, S. Sakamoto, K. Yamaguchi, J.-P. Sauvage, *J. Am. Chem. Soc.* **2003**, *125*, 5717–5725; c) L. Raehm, J.-M. Kern, J.-P. Sauvage, C. Hamann, S. Palacin, J.-P. Bourgoin, *Chem. Eur. J.* **2002**, *8*, 2153–2162; d) M. E. Padilla-Tosta, O. D. Fox, M. G. B. Drew, P. D. Beer, *Angew. Chem.* **2001**, *113*, 4365–4369; *Angew. Chem. Int. Ed.* **2001**, *40*, 4235–4239; e) V. Balzani, A. Credi, S. J. Langford, F. M. Raymo, J. F. Stoddart, M. Venturi, *J. Am. Chem. Soc.* **2000**, *122*, 3542–3543; f) F. Ibukuro, M. Fujita, K. Yamaguchi, J.-P. Sauvage, *J. Am. Chem. Soc.* **1999**, *121*, 11014–11015; g) M. Fujita, *Acc. Chem. Res.* **1999**, *32*, 53–61.
- [5] a) S. Tashiro, M. Tominaga, T. Kusukawa, M. Kawano, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem.* **2003**, *115*, 3389–3392; *Angew. Chem. Int. Ed.* **2003**, *42*, 3267–3270; b) M. Tominaga, S. Tashiro, M. Aoyagi, M. Fujita, *Chem. Commun.* **2002**, 2038–2039; c) M. Aoyagi, K. Biradha, M. Fujita, *J. Am. Chem. Soc.* **1999**, *121*, 7457–7458.
- [6] a) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3498; b) O. Mamula, A. von Zelewsky, G. Bernardinelli, *Angew. Chem.* **1998**, *110*, 302–305; *Angew. Chem. Int. Ed.* **1998**, *37*, 289–293; c) P. L. Jones, K. J. Byrom, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Chem. Commun.* **1997**, 1361–1362; d) B. Hasenknopf, J.-M. Lehn, B. O. Kneisel, G. Baum, D. Fenske, *Angew. Chem.* **1996**, *108*, 1987–1990; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1838–1840.
- [7] a) F. A. Cotton, P. Lei, C. Lin, C. A. Murillo, X. Wang, S.-Y. Yu, Z.-X. Zhang, *J. Am. Chem. Soc.* **2004**, *126*, 1518–1525; b) Y. K. Kryschenko, S. R. Seidel, D. C. Muddiman, A. I. Nepomuceno, P. J. Stang, *J. Am. Chem. Soc.* **2003**, *125*, 9647–9652; c) L. Pirondini, F. Bertolini, B. Cantadori, F. Uguzzoli, C. Massera, E. Dalcanale, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4911–4915; d) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; e) S. J. Park, J.-I. Hong, *Chem. Commun.* **2001**, 1554–1555; f) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509–518; g) O. D. Fox, M. G. B. Drew, P. D. Beer, *Angew. Chem.* **2000**, *112*, 139–144; *Angew. Chem. Int. Ed.* **2000**, *39*, 135–140; h) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter, P. J. Stang, *Nature* **1999**, *398*, 796–799; i) A. Ikeda, M. Yoshimura, H. Udzu, C. Fukuhara, S. Shinkai, *J. Am. Chem. Soc.* **1999**, *121*, 4296–4297; j) O. D. Fox, N. K. Dalley, R. G. Harrison, *J. Am. Chem. Soc.* **1998**, *120*, 7111–7112; k) T. Kusukawa, M. Fujita, *Angew. Chem.* **1998**, *110*, 3327–3329; *Angew. Chem. Int. Ed.* **1998**, *37*, 3142–3144; l) P. Jacopozzi, E. Dalcanale, *Angew. Chem.* **1997**, *109*, 665–667; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 613–615.
- [8] a) M. Ferrer, M. Mounir, O. Rossell, E. Ruiz, M. A. Maestro, *Inorg. Chem.* **2003**, *42*, 5890–5899; b) C. A. Schalley, T. Müller, P. Linnartz, M. Witt, M. Schäfer, A. Lützen, *Chem. Eur. J.* **2002**, *8*, 3538–3551; c) M. Schweiger, S. R. Seidel, A. M. Arif, P. J. Stang, *Inorg. Chem.* **2002**, *41*, 2556–2559; d) A. Sautter, D. G. Schmid, G. Jung, F. Würthner, *J. Am. Chem. Soc.* **2001**, *123*, 5424–5430; e) T. Bark, M. Düggele, H. Stoeckli-Evans, A. von Zelewsky, *Angew. Chem.* **2001**, *113*, 2924–2927; *Angew. Chem. Int. Ed.* **2001**, *40*, 2848–2851; f) S. B. Lee, S. Hwang, D. S. Chung, H. Yun, J.-I. Hong, *Tetrahedron Lett.* **1998**, *39*, 873–876.
- [9] a) T. Yamamoto, A. M. Arif, P. J. Stang, *J. Am. Chem. Soc.* **2003**, *125*, 12309–12317; b) S. Hiraoka, T. Yi, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2002**, *124*, 14510–14511; c) G. Ma, Y. S. Jung, D. S. Chung, J.-I. Hong, *Tetrahedron Lett.* **1999**, *40*, 531–534.
- [10] a) O. Mamula, F. J. Monlien, A. Porquet, G. Hopfgartner, A. E. Merbach, A. von Zelewsky, *Chem. Eur. J.* **2001**, *7*, 533–539; b) P. N. W. Baxter, R. G. Khoury, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4140–4148.
- [11] P. N. W. Baxter, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur. J.* **2000**, *6*, 4510–4517.
- [12] a) M. Aoyagi, S. Tashiro, M. Tominaga, K. Biradha, M. Fujita, *Chem. Commun.* **2002**, 2036–2037; b) Y. Yamanoi, Y. Sakamoto, T. Kusukawa, M. Fujita, S. Sakamoto, K. Yamaguchi, *J. Am. Chem. Soc.* **2001**, *123*, 980–981.
- [13] S. J. Park, D. M. Shin, S. Sakamoto, K. Yamaguchi, Y. K. Chung, M. S. Lah, J.-I. Hong, *Chem. Commun.* **2003**, 998–999.
- [14] J. C. Sherman, C. B. Knobler, D. J. Cram, *J. Am. Chem. Soc.* **1991**, *113*, 2194–2204.
- [15] In $[\text{D}_6]\text{DMSO}$, the interclipped capsule **3** is formed as a sole adduct. This indicates that solvent polarity is not the only factor that alters the equilibrium. Changes in the solvent system may affect the donor ability of solvent molecules and/or the solvation of charged molecules.
- [16] A sharp singlet in the ^{19}F NMR spectrum suggests that the weakly coordinating counterion OTf^- is rapidly and freely exchangeable between the two supramolecular species (see Supporting Information).

- [17] Crystal data for an interclipped capsule (**3b**): $C_{114}H_{105}F_{12}N_4O_{24}P_4Pt_2S_{12}$, $M_r = 3041.80$, colorless crystal $0.50 \times 0.40 \times 0.22$ mm³, tetragonal $I4_1/a$, $a = b = 36.7746(7)$, $c = 48.2779(12)$ Å, $V = 65290(2)$ Å³, $Z = 16$, $\rho_{\text{calcd}} = 1.238$ mg cm⁻³, $F(000) = 24400$, $\mu(\text{MoK}\alpha, \lambda = 0.71073 \text{ \AA}) = 1.972$ mm⁻¹, $T = 293(2)$ K, $2\theta_{\text{max}} = 50.70^\circ$. Data were recorded by using an Enraf-Nonius Kappa-CCD equipped with a graphite crystal incident-beam monochromator Lp ; reflections collected 44682, unique reflections 28334, observed reflections 8090 [$I > 2\sigma(I)$]. The structure was solved by employing direct methods and refined by full-matrix least-squares calculations by using SHELX-97. The final R values were $R_1 = 0.1585$, $wR_2 = 0.4550$ [$I > 2\sigma(I)$], $R_1 = 0.3630$, $wR_2 = 0.5217$ (all data). CCDC-222188 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).
- [18] The addition of nonvolatile solvents such as *p*-xylene is crucial for the formation of a stable, single crystal. The existence of these solvent molecules in and/or out of the cavity of a nanoscale capsule may prevent the collapse of the crystal lattice.
- [19] It was not possible to calculate the equilibrium ratios at 353 K and 363 K from the integral of the H_o and H_o' peaks because the signals overlap. We could, however, deduce from the integral ratios of H_e and H_e' that more than 97% of the adduct exists as an intracapped bowl **4a** at 363 K.
- [20] To determine the structures of the supramolecular capsule **3** and bowl **4**, electrospray ionization mass spectrometry (ESI-MS) was performed at the ion-source temperatures 25 and 60°C (see Supporting Information). The relative intensities of $[\mathbf{3a} - 3\text{CF}_3\text{SO}_3]^{3+}$ and $[\mathbf{3a} - 5\text{CF}_3\text{SO}_3]^{5+}$ signals increased at the lower ion-source temperature. This indicates that the relative amount of interclipped adduct **3** increases at lower temperature, which is consistent with our former assumption.
- [21] H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, Wiley-VCH, Weinheim, **1991**, pp. 263–291.

Received: August 4, 2004

Published online: November 17, 2004