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Solution Behavior of Nanosize Coordination Molecular Capsules

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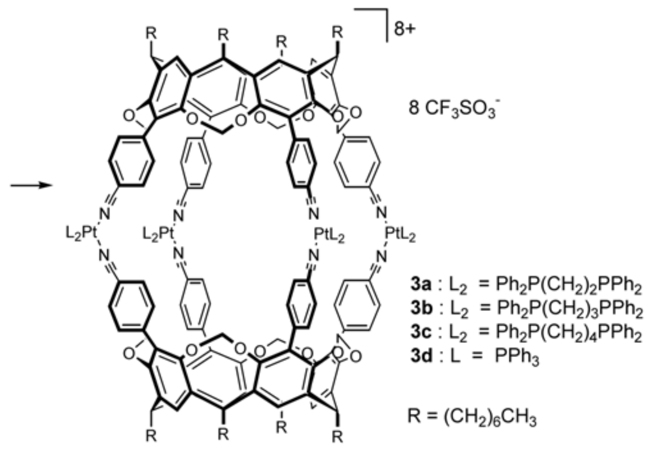
Container molecules have been assembled through covalent bonds as well as non-covalent bond interactions. The former examples mostly developed by Cram's group are cavitand,[1] hemicarcerand,[2] and carcerand,[3] which are classified by the energy-barrier for the entering or emitting of guest through the shell of container molecule. The latters are self-assembled molecular capsules (SMC) held together by hydrogen bond or metal-ligand interaction.[4]

The SMCs by metal-ligand interaction were constructed by ordered association of organic ligands and metal ions in convergent manner.[5,6] Recently we reported the efficient synthesis of deep-cavity tetracyanocavitand **1** by drastically reducing its synthetic steps.[7] Here we report the unusual solution behaviors of SMC **3a-d**, having a nanosize cavity utilizing cyano-Pt interaction.

Square planar *cis*-Pt bis(triflate) complexes **2a-d** were prepared by the reaction of the corresponding $PtCl_2$ complex with AgOTf.[6b,8] SMCs **3a-d** were assembled by mixing cavitand **1** with **2a-d** in a 1 : 2 molar ratio at room temperature in a nonpolar solvent such as $CHCl_3$, CH_2Cl_2, or tetrachloroethane.



Scheme 1. Synthesis of SMCs **3a-3d**.

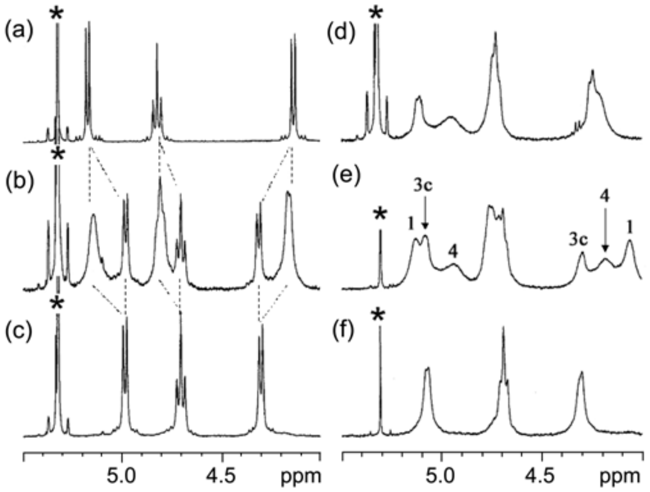
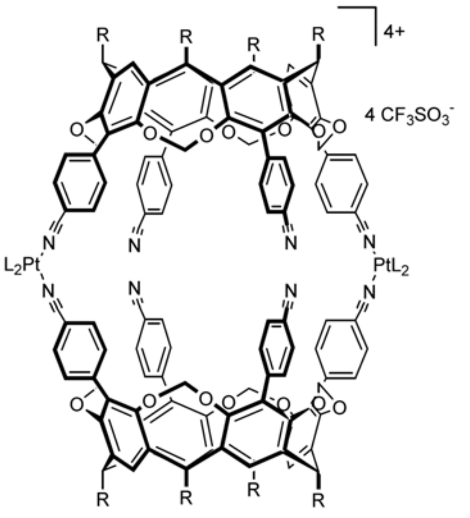


Figure 1. Partial ^1H NMR spectra ([**1**] = 3 mM, 400 MHz, 298K, a-d in CD_2Cl_2, e-f in $CDCl_2CDCl_2$): (a) **1**, (b) [**1**] : [**2a**] = 1 : 1, (c) **3a** ([**1**] : [**2a**] = 1 : 2), (d) [**1**] : [**2c**] = 1 : 2, (e) [**1**] : [**2c**] = 1 : 1, (f) **3c** ([**1**] : [**2c**] = 1 : 2). Symbols (*) designate the proton of residual CH_2Cl_2.

Figure 1 shows the partial ^1H NMR spectra comparing the changes of chemical shifts of dioxymethylene (doublets at 5.22 and 4.17 ppm) and of methine (triplet at 4.82 ppm) hydrogens of tetracyanocavitand **1** or those of SMC **3** upon metal-ligand interaction. As reported, when mixing 1 : 1 of **1** and **2a** in CD_2Cl_2 at 25 °C, these proton peaks of free cavitand **1** and SMC **3a** (doublets at 4.98 and 4.30 ppm, triplet at 4.70 ppm) appeared separately in a 1 : 1 ratio (Figure 1b). When the ratio of **1** : **2a** reached 1 : 2, the peaks of free cavitand **1** disappeared completely and only those of SMC **3a** remained, as expected (Figure 1c)[7].

The formation process of SMC **3c** was observed by ^1H NMR spectra in $CDCl_2CDCl_2$ at 25 °C. For a 1 : 1 mixture of cavitand **1** and metal complex **2c**, the two peaks of dioxymethylene protons for free **1** were separated into three sets of peaks in a 1 : 1 : 1 ratio at 5.13, 4.06 ppm for free **1**, 5.08, 4.29 ppm for SMC **3c**, and 4.94, 4.18 ppm for the unknown compound (Figure 1e). At 363 K, these peaks were coalesced and then reappeared when cooled to 298 K. But



4 : L_2= -$PPh_2(CH_2)_4PPh_2$-
R = $(CH_2)_6CH_3$

Scheme 2

for 1 : 2 mixture of cavitand **1** and metal complex **2c**, only the peaks for SMC **3c** appeared (Figure 1f).

The structure of unknown compound was assigned to the across-bridged SMC **4** on the bases of symmetry of **4** and the 1 : 1 : 1 equilibrium stoichiometry (Figure 1e). The detection of SMC **4** implies that the energy barrier for the equilibrium between **4** and **3c** is not substantial. But it is quite probable that SMC **4** was formed first, and then transformed to the thermodynamic product SMC **3c**.

The solvent effects on the formation of SMC are summarized in Table 1. The solvent effects on the formation of SMC **3a** and SMC **3b** are similar. ^{1}H NMR spectrum of 1 : 2 mixture of **1** and **2c** in CD_2Cl_2 or $CDCl_3$ shows oligomeric product (Figure 1d). When it was taken in $CDCl_2CDCl_2$, only SMC product was observed (Figure 1f). Overall, the solvent effect for the formation of SMC **3c** decreases in the order: $CDCl_2CDCl_2 > CDCl_3 \geq CD_2Cl_2$. In case of a 1 : 2 mixture of **1** and **2d**, SMC **3d** was not observed in CD_2Cl_2 or $CDCl_3$. However, in a 1 : 2 mixture of **1** and **2d** in $CDCl_2CDCl_2$, SMC **3d** was observed together with oligomers. It is presumable that the larger nonpolar solvent, especially tetrachloroethane, could template and stabilize SMC **3** better.

Table 1. Influence of metal complex **2a-d** and solvents on the formation of Self-Assembled Molecular Capsule (SMC) **3** at 298 K

SMC	Solvent	**1** : **2** = 1 : 1	**1** : **2** = 1 : 2
3a (**1** + **2a**)	CD_2Cl_2	**1** + SMC **3a**	SMC **3a**
3a (**1** + **2a**)	$CDCl_3$	**1** + SMC **3a**	SMC **3a**
3a (**1** + **2a**)	TCE	**1** + SMC **3a**	SMC **3a**
3b (**1** + **2b**)	CD_2Cl_2	**1** + SMC **3b**	SMC **3b**
3b (**1** + **2b**)	$CDCl_3$	**1** + SMC **3b**	SMC **3b**
3b (**1** + **2b**)	TCE	**1** + SMC **3b**	SMC **3b**
3c (**1** + **2c**)	CD_2Cl_2	O	O
3c (**1** + **2c**)	$CDCl_3$	O	O
3c (**1** + **2c**)	TCE	**1** + **4** + SMC **3c**	SMC **3c**
3d (**1** + **2d**)	CD_2Cl_2	O	O
3d (**1** + **2d**)	$CDCl_3$	O	O
3d (**1** + **2d**)	TCE	O	SMC **3d** + O

TCE = $CDCl_2CDCl_2$, SMC = Self-Assembled Molecular Capsule, O = Oligomer.

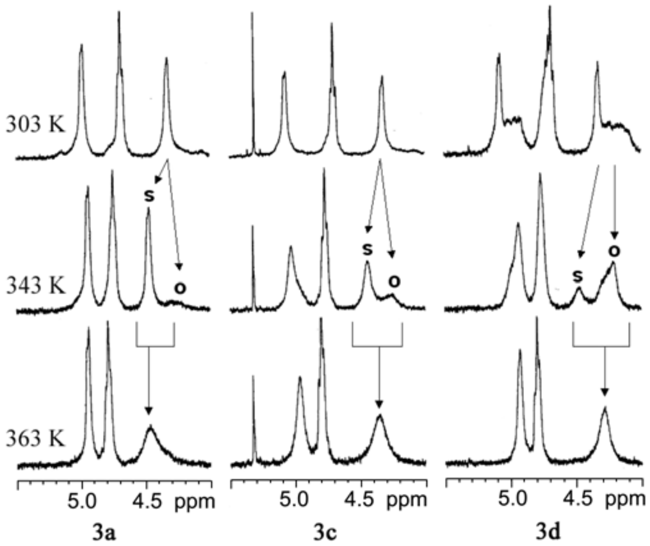


Figure 2. Partial ^{1}H NMR spectra of SMC **3a**, **3c**, and **3d** in $CDCl_2CDCl_2$ at various temperatures. Symbols designate the proton of (s) SMC **3a**, **3c** and **3d**, (o) oligomer.

The influence of the chelate ring size of **2a-2d** is also summarized in Table 1. Pt(II) prefers the square-planar coordination sphere. Table 1 shows that the thermodynamic stability of SMC **3** depends on the chelate size on Pt and decreases in the order: **3a**~**3b** > **3c** >> **3d**, which is similar to the results of Dalcanale *et al.*[6b] In the case of SMC **3d**, its additional structural flexibility on metal part might also cause its low stability.

The relative thermodynamic stabilities of SMC **3a**, **3c**, and **3d** were also observed by VT ^{1}H NMR experiment. As Figure 2 shows, the peaks of the inner hydrogen of dioxymethylene were split into two peaks at 343 K, and then coalesced into a broad singlet at 363 K. The ratios of SMC **3a**, **3c** and **3d**, and the corresponding oligomers at 343 K, are about 80 : 20, 70 : 30, and 25 : 75, respectively, which reconfirms the relative stability order: **3a** > **3c** >> **3d**.

In conclusion, the solution behaviors of self-assembled molecular capsules (SMC) **3** by Pt-cyano interaction were characterized in nonpolar solvents. The stability of nano-size SMC **3** depends on the polarity and size of solvent, temperature, as well as, the chelate on Pt complex.

Experimental Section

Solvents and all commercially available reagents were used without any purification. ^{1}H NMR spectra were recorded at 400 MHz on a Bruker Avance 400 spectrometer. Infrared spectra were recorded on a Mattson 3000 spectrometer.

SMC 3a: ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 7.92-7.17 (m, 120H, PPh_2, CNAr*H* and Ar*H*), 4.98 (d, 8H, J = 7.2 Hz, outer OCH_2O), 4.70 (t, 8H, J = 7.6 Hz, methine), 4.30 (d, 8H, J = 7.2 Hz, inner OCH_2O), 2.87 (bd, 16H, J = 19.6 Hz, PCH_2CH_2P), 2.32 (bs, 16H $CH_2(\mathrm{CH_2})_5\mathrm{CH_3}$), 1.47-1.33 (m, 80H, $(CH_2)_5\mathrm{CH_3}$), 0.92 (t, 24H, J = 6.8 Hz, $(\mathrm{CH_2})_6CH_3$).

SMC 3b: ^{1}H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ = 7.77-6.98 (m, 120H, PPh_2, CNAr*H* and Ar*H*), 5.07 (d, 8H, J = 7.2 Hz, outer OCH_2O), 4.70 (t, 8H, J = 7.6 Hz, methine), 4.22 (d, 8H, J = 7.2 Hz, inner OCH_2O), 3.02 (bs, 8H, $\mathrm{PCH_2}CH_2\mathrm{CH_2P}$), 2.32 (t, 16H, J = 8.0 Hz, $\mathrm{P}CH_2\mathrm{CH_2}CH_2\mathrm{P}$), 1.46-1.32 (m, 80H, $(CH_2)_5\mathrm{CH_3}$), 0.91 (t, 24H, J = 6.4 Hz, $(\mathrm{CH_2})_6CH_3$); ^{19}F NMR (282.4 MHz, CD_2Cl_2, 25 °C): δ = −0.4 (24F, $CF_3CO_3^-$).

SMC 3c: ^{1}H NMR (400MHz, $CDCl_2CDCl_2$, 25 °C): δ = 7.64-6.93 (m, 120H, PPh_2, CNAr*H* and Ar*H*), 5.07 (bd, 8H, outer OCH_2O), 4.68 (bt, 8H, methine), 4.30 (bd, 8H, inner OCH_2O), 2.70 (bs, 16H, $\mathrm{PCH_2}CH_2CH_2\mathrm{CH_2P}$), 2.15 (bm, 16H, $\mathrm{P}CH_2\mathrm{CH_2CH_2}CH_2\mathrm{P}$), 1.45-1.30 (m, 80H, $(CH_2)_5\mathrm{CH_3}$), 0.90 (m, 24H, $(\mathrm{CH_2})_6CH_3$).

SMC 3d: A clear NMR spectrum was not obtained due to mixed oligomeric sepcies.

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