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Self-assembled nanoscale capsules between resorcin[4]arene derivatives and Pd(II) or Pt(II) complexes

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Nanoscale molecular capsules have been prepared by self-assembly of resorcin[4]arene derivatives and Pd(II) or Pt(II) complexes; the positively charged *N*-alkylpyridinium derivatives are encapsulated inside capsules due to strong cation–π interactions.

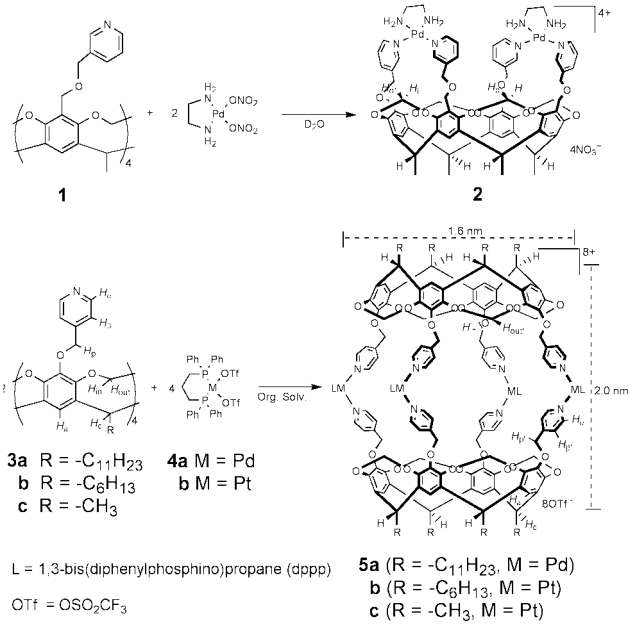
The formation of self-assembled superstructures has received a great deal of attention in recent years. Two main approaches have been widely used to construct supermolecules using intermolecular interactions between building blocks. One involves using hydrogen bonding interactions between the complementary binding sites.[1] The other approach is to employ metal–ligand interactions. Metal-induced self-assembly is a flourishing area of study in the field of host–guest and supramolecular chemistry. There are many examples of metal-mediated self-assembly to form squares,[2] helices,[3] grids,[4] catenanes,[5] cylinders,[6] circular helicates[7] and cages.[8]

Recently we reported that an intramolecularly assembled structure **2** was constructed by addition of two equivalents of $(en)Pd(NO_3)_2$ to a suspension of **1** in aqueous solution (Scheme 1).[9] Molecular models show that pyridyl groups of **3** with one fewer carbon compared to **1**, however, cannot easily get close enough to form an intramolecularly organized structure *via* Pd(II) or Pt(II) complexation. Herein we describe the formation of nanoscale cage-like complexes composed of two resorcin[4]arene derivatives and four Pd^{II} or Pt^{II} square planar precursors, and the complexation of *N*-alkylpyridinium derivatives in the organic phase.

Capsules are instantly formed by simple addition of two equivalents of $Pd(dppp)(OTf)_2$ to acetone, CH_2Cl_2 or $CHCl_3$ solutions of resorcin[4]arene derivatives **3a–c**† having four pyridine units as pendent groups (Scheme 1). For **2**, the bridge methylene protons split into two sets of signals in the ^1H NMR spectrum since $H_{i'}$ and $H_{o'}$ exist in the shielding region between two pyridine ligands interacting with a Pd(II) ion and move far upfield compared to H_i and H_o.[9] In the present case, however, the bridge methylene protons ($H_{in'}$ and $H_{out'}$) do not divide into two sets [Fig. 1(e)]. Both ^1H and ^{13}C NMR spectra are in accord with the D_{4h} symmetric structure of **5** and the assignments are fully supported by two-dimensional NMR measurements. In particular, a ^1H NMR titration study clearly shows capsule formation. When **3a** and **4a** are mixed in a 1 : 1 molar ratio, a mixture of the capsule **5a**† and free **3a** is obtained. Moreover, when an excess amount of **4a** is added, **5a** and unreacted **4a** are present (Fig. 1). This means that a 1 : 2 adduct is formed as the sole product.

The molecular weight estimated by vapor pressure osmometry (VPO) of a CH_2Cl_2 solution containing **3a** and **4a** in a 2 : 4 molar ratio (6230 ± 590) is consistent with the molecular weight for the dimer **5a** (6426). Moreover, electrospray ionization mass spectrometry (ESI-MS) clearly shows the formation of **5b** when a $CHCl_3$ solution containing **2b** and **3b** in a 2 : 4 molar ratio was examined: $[M - 2CF_3SO_3^-]^{2+}$ (2961.99), $[M - 3CF_3SO_3^-]^{3+}$ (1928.83) and $[M - 4CF_3SO_3^-]^{4+}$ (1406.44).‡ Molecular modeling shows that the cavity of **5** has nanoscale dimensions of 16 × 20 Å.[10]

Several neutral guest molecules such as adamantane, anthracene, phenanthrene and pyrene show no ^1H NMR spectroscopic signs of encapsulation within the capsule. This indicates either that there is no driving force for the guest encapsulation or the guests are too small to be encapsulated due to the large portals of the capsule through which these guests can permeate. However, addition of a positively charged guest such as 1-methyl-4-phenylpyridinium (OTf^- salt) **6** and methylviologen ($2OTf^-$ salt) **7** to an acetone-d_6 solution of **3a** followed by addition of 2 equivalents of **4a** to the resulting mixture gave two sets of separate ^1H NMR peaks for the free and bound



Scheme 1

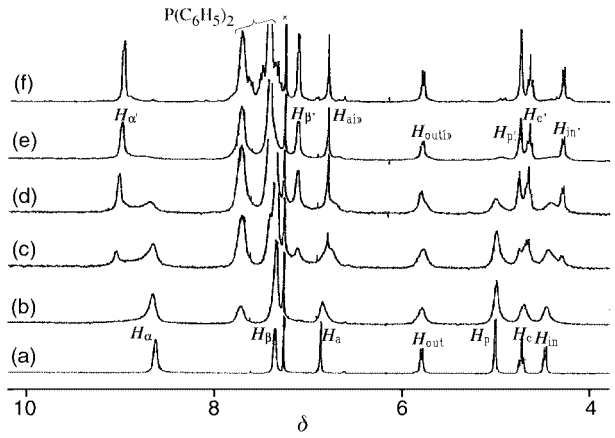


Fig. 1 Monitoring capsule formation by ^1H NMR spectroscopy (300 MHz, $CDCl_3$, 300 K). (a) free **3a**; (b) **3a**:**4a** = 2:1; (c) **3a**:**4a** = 2:2; (d) **3a**:**4a** = 2:3; (e) **3a**:**4a** = 2:4; (f) **3a**:**4a** = 2:5 molar ratio. A signal at δ 7.28 from $CDCl_3$ is marked by an asterisk.

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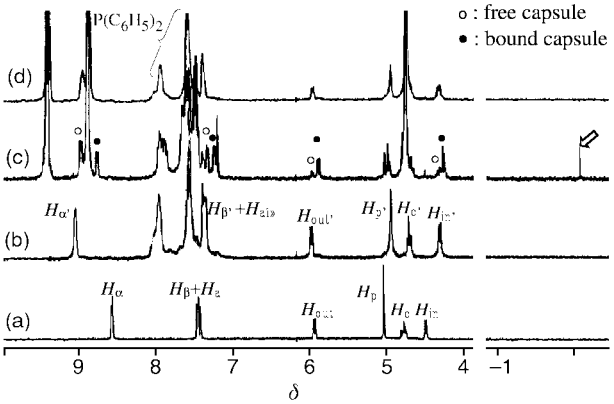

Fig. 2 Portion of the ^{1}H NMR spectra (300 MHz, acetone-d_6, 300 K); (a) free **3a**; (b) capsule **5a** formed from **3a**:**4a** = 2:4; (c) *ca.* 10 equiv. **7** added to **3a** and then 2 equiv. **4a** was added; (d) *ca.* 10 equiv. **7** was added to **5a**. The methyl group of the encapsulated guest is indicated by an arrow.

capsules.[11] This peak separation indicates that the decomplexation or guest-exchange rate is slow with respect to the ^{1}H NMR time scale. In addition, the integration ratio of the bound capsule and encapsulated guest resonances indicated a highly symmetric 1:1 complex. Particularly, NCH_3 protons of **7** move *ca.* 6.8 ppm upfield, appearing at δ −2.08,§ which presumably indicates that **7** is encapsulated such that the methyl group points towards the shielding region of the aromatic cavity at the end of the long axis of the capsule. As expected from the nearly irreversible Pd–pyridine bond formation in organic solvents, when **7** was added after the capsule formation, no spectroscopic signs of encapsulation were detected except that the pyridine's α-proton shifted slightly in the upfield direction (Fig. 2).¶ In order to investigate the behavior of the counter ions, the ^{19}F NMR spectrum was examined and showed only one signal at δ −77 in the spectra of **5a** and **5a** containing **7**; this indicates that there is not a slow exchange between triflate ions inside and outside of the cage. We also observed the release of the encapsulated **7** from the capsule in acetone-d_6 upon heating at 35 °C in the sealed NMR tube. The first-order approximation gives a guest-releasing rate constant of 4.5×10^{-6} s^{-1}. This means that guest release occurs slowly with a half-life of 43 h at 308 K. These phenomena indicate that **7** was complexed inside **3a**, most probably due to the cation–π interaction, and then if **4a** was added, properly positioned **7** was entrapped in the forming capsule **5a**.¶

In summary, we have constructed nanoscale self-assembled molecular capsules instead of an intramolecularly organized structure between properly designed resorcin[4]arene derivatives having relatively rigid pendent pyridine groups and square planar metal complexes. The positively charged *N*-methylpyridinium derivatives turn out to be encapsulated by cation–π interactions. Further studies will explore the potential for the use of nanoscale capsules as selective reaction chambers for chemical reaction catalysis.¶

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Notes and references

† **3a**: δ_H (300 MHz, $CDCl_3$) 8.61 (d, *J* 5.89 Hz, 8H), 7.32 (d, *J* 5.89 Hz, 8H), 6.88 (s, 4H), 5.79 (d, *J* 7.11 Hz, 4H), 5.01 (s, 4H), 4.75 (t, *J* 7.92 Hz, 4H), 4.49 (d, *J* 7.12 Hz, 4H), 2.22 (br, 8H) 1.4–1.1 (br m, 72H), 0.90 (t, *J* 6.58 Hz, 12H); δ_C (75 MHz, $CDCl_3$) 149.69, 147.97, 147.01, 144.09, 139.07, 121.39, 114.69, 99.45, 73.37, 36.91,31.92, 29.83, 29.71, 29.40, 27.91, 22.68, 14.11; FAB-MS (NBA) *m*/*z* 1581.9962 (M + H$^+$) (calc. 1581.9920).

3b: δ_H (300 MHz, $CDCl_3$) 8.61 (d, *J* 5.18 Hz, 8H), 7.33 (d, *J* 5.37 Hz, 8H), 6.88 (s, 4H), 5.79 (d, *J* 7.12 Hz, 4H), 5.01 (s, 4H), 4.75 (t, *J* 7.93 Hz, 4H), 4.49 (d, *J* 7.13 Hz, 4H), 2.22 (br, 8H) 1.4–1.1 (br m, 32H), 0.92 (t, *J* 6.47 Hz, 12H); δ_C (75 MHz, $CDCl_3$) 149.62, 147.98, 146.99, 144.08, 139.10, 122.00, 113.98, 99.44, 73.36, 36.37, 31.85, 29.78, 29.44, 27.84, 22.62, 14.34 ; ESI-MS *m*/*z* 1301.6 (M + H$^+$).

3c: δ_H (300 MHz, $CDCl_3$) 8.61 (d, *J* 5.85 Hz, 8H), 7.33 (d, *J* 5.71 Hz, 8H), 7.02 (s, 4H), 5.81 (d, *J* 7.12 Hz, 4H), 5.1–4.9 (m, 12H), 4.50 (d, *J* 7.13 Hz, 4H), 2.22 (br, 8H) 1.78 (t, *J* 7.42 Hz, 12H); δ_C (75 MHz, $CDCl_3$) 149.56, 147.66, 147.15, 143.97, 139.99, 121.54, 114.18, 99.45, 73.40, 31.23, 15.82; FAB-MS (NBA) *m*/*z* 1021.3663 (M + H$^+$) (calc. 1021.3660).

5a: δ_H (300 MHz, $CDCl_3$) 8.95 (d, *J* 5.12 Hz, 16H), 7.72 (br, 32H), 7.42 (br, 48H), 7.12 (d, *J* 5.36 Hz, 16H), 6.80 (s, 8H), 5.79 (d, *J* 6.96 Hz, 4H), 4.76 (s, 16H), 4.60 (t, *J* 7.60 Hz, 8H), 4.30 (d, *J* 7.04 Hz, 8H), 3.22 (br, 16H), 2.32 (m, 8H), 2.15 (br, 16H), 1.23 (br, 144H), 0.85 (t, *J* 6.56 Hz, 24H); δ_C (75 MHz, $CDCl_3$) 150.9, 150.2, 147.6, 144.3, 138.9, 133.2, 132.2, 129.5, 125.7, 122.8, 121.0 (q, *J* 318 Hz, CF_3), 114.6, 99.5, 72.3, 36.9, 31.9, 29.8, 29.7, 29.6, 29.4, 27.9, 22.7, 21.6, 17.7, 14.1.

‡ When **5c** formed from gentle heating of a $CHCl_3$–MeOH (10:1, v/v solution of **3c** and **4b** in 1:2 molar ratio was examined by ESI-MS, [M − *n*$CF_3SO_3^-$]$^{n+}$ (*n* = 2,3,4) ion peaks were also clearly observed at *m*/*z* 2682.21, 1739.52 and 1266.74, respectively.

§ NCH_3 protons of the encapsulated guest **6** appear at δ −2.09.

¶ Addition of 1,4-dimethylpyridinium triflate, which is small enough to freely pass in and out of the cavity, either before or after capsule formation, results in two sets of separate ^{1}H NMR peaks for the free and bound capsules. NCH_3 protons of the encapsulated 1,4-dimethylpyridinium triflate also appear at δ −2.08. This constitutes strong evidence for cation–π interactions in the encapsulation process. According to molecular modeling[10] and ^{1}H NMR integration, the interior of **5a** can accommodate two molecules of 1,4-dimethylpyridinium triflate. The association constant (K_a) can be estimated from the ratio of peak intensity of free and bound to be 1180 dm^6 mol^{-2}.

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