Water-soluble supramolecular bowls formed by intra-clipping of resorcin[4]arene-based ligands with Pd(II) ions†

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Bowl-shaped superstructures have been constructed by intra-clipping of resorcin[4]arene derivatives with two equivalents of (en)Pd(NO3)2 in water. The binding phenomena of the aromatic carboxylates were proven to be both enthalpically and entropically favoured.

There is a great deal of interest in self-assembled superstructures, with particular focus being placed on metal-induced supramolecules such as molecular triangles, squares, helicates, grids, catenanes, cylinders, and cages. The relative lability of metal–ligand bonds allows facile routes for interconversion favouring formation of the thermodynamically more stable isomer. Thus, the structures of supramolecules constructed with the same metals and ligands could be tuned by simple changes of counter ions, metal–ligand ratios, and reaction conditions such as concentrations, temperatures, and solvent systems.

We have been extensively investigating the formation of superstructures composed of cis-protected square planar M(dpdp)(OTf)2 (M = Pd, Pt) and resorcin[4]arene derivatives having four pyridine (Py) or pyrimidine units as pendant groups. Recently, we found that when ligand 1a and two equivalents of Pd(dpdp)(OTf)2 were mixed, both intra-clipped bowl 2c and inter-clipped capsule 3c were formed in a dynamic manner in nitromethane, whereas the inter-clipped capsule 3c was constructed as the sole adduct in a CDCl3–CD3OD = 10:1 (v/v) solution. Herein, we describe the exclusive formation of the intra-clipped structure 2a (or 2b) from resorcin[4]arene-based ligand 1a (or 1b) and water-soluble Pd(II) ions, as well as their complexation behaviors with various aromatic carboxylate guests in aqueous media (Scheme 1).

When a suspended aqueous solution of ligand 1a (or 1b) and two equiv. (en)Pd(NO3)2 was heated at 80 °C for 20 min, a clear solution was obtained. 1H NMR spectroscopic analysis showed only the formation of a C2v symmetric superstructure, which was mainly deduced from the splitting of the bridging methylene protons into two sets of signals. Since protons H1 and H2 exist in the shielding region between the two pyridine ligands, they are expected to move further upfield than H1 and H2.

Additional support for the formation of the proposed supramolecular bowl 2a (or 2b) was obtained by coldspray ionization mass spectrometric (CSI-MS) spectra: [2a − NO3]−2 (1538.2), [2a − 2NO3]−2 (738.1), [2b − NO3]−2 (1538.2), [2b − 2NO3]−2 (738.1).

The structure of the intra-clipped supramolecular bowl 2b was further corroborated by X-ray crystallographic analysis (Fig. 1). A single crystal suitable for X-ray structure analysis was obtained by slow diffusion of ethanol into an aqueous methanol solution of 2b at ambient temperature for 4 days. The crystal structure of 2b clearly demonstrates that 1b is clipped by two Pd(II) ions. Each Pd(II) has a square planar geometry with Pd···NNO distances in the range of 2.015(5)–2.041(6) Å, and NNO–Pd–NNO angles are 90.1(2) and 91.8(2)° which are close to the ideal value of 90°. The Pd···Pd distance is 7.10 Å.

Supramolecular bowl 2b crystallized with a single methanol molecule entrapped within its cavity. And one of four nitrate ions stays between two Pd(II) ions by ionic interaction. The methyl group of the entrapped methanol molecule is surrounded by four aromatic rings with distances of 3.6–3.7 Å measured between the centroid of the aromatic rings and the carbon of the methanol guest. This clearly shows the existence of a CH–π (aromatic) interaction. And the disordered OH group of the entrapped methanol molecule hydrogen bonds to an nitrate ion

† Electronic supplementary information (ESI) available: spectral data. See http://www.rsc.org/suppdata/cc/b2/b212855a/
situated between the clipping Pd(II) ions. The distances between the three distinctive disordered methanol O sites and the nitrate O are in the range of 2.6–3.0 Å (O11m (0.49 site occupancy)–O1m(NO$_3^-$) 2.98 Å; O12m (0.25 site occupancy)–O1m(NO$_3^-$) 2.68 Å; O13m (0.25 site occupancy)–O3m(NO$_3^-$) 2.61 Å). Therefore, we presume that there is a hydrogen bond between the methanol hydrogen and the nitrate oxygen.

Since supramolecular bowls (2a and 2b) have intramolecularly organized recognition sites induced by metal-clipping, their complexation behaviors were investigated with several aromatic carboxylates in aqueous phase. The host–guest complexation with supramolecular bowl 2a (or 2b) was demonstrated by an isothermal titration calorimetry (ITC) experiment at 30 °C in water. Binding constants as well as thermodynamic parameters controlling the complexation process between 2a (or 2b) and several aromatic acid sodium salts were obtained (Table 1).

**Table 1** Binding constants ($\times 10^4$ M$^{-1}$) and thermodynamic parameters (kcal mol$^{-1}$) for complexation of aromatic carboxylates with Pd(II)-clipped supramolecular bowls (2a or 2b) at 30 °C in water.$^a$

<table>
<thead>
<tr>
<th></th>
<th>$K_a$</th>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$T \Delta S^\circ$</th>
<th>$2a$</th>
<th>$2b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid sodium salt</td>
<td>4.66</td>
<td>-2.60</td>
<td>3.84</td>
<td>2.08</td>
<td>-1.87</td>
<td>4.07</td>
</tr>
<tr>
<td>p-Toluic acid sodium salt</td>
<td>17.6</td>
<td>-1.48</td>
<td>5.73</td>
<td>2.74</td>
<td>-2.08</td>
<td>4.04</td>
</tr>
<tr>
<td>p-Anisic acid sodium salt</td>
<td>10.2</td>
<td>-1.93</td>
<td>4.96</td>
<td>2.85</td>
<td>-2.73</td>
<td>3.42</td>
</tr>
</tbody>
</table>

The complexation processes are both enthalpically and entropically favoured. Both the enthalpy gain from electrostatic and hydrophobic interactions, and the entropy gain from desolvation cooperatively contribute to the binding of the anionically charged guests. Comparison of binding constants between 2a and 2b showed that 2a had stronger binding affinities toward aromatic anionic guests than 2b. This might originate partially from the steric hindrances between the inward pointing (en)Pd moieties in 2b and the aromatic guests, which was inferred from the crystal structure of 2b.

In order to elucidate the binding mode, complexation-induced chemical shift changes were measured with 2a and p-toluic acid sodium salt (Fig. 2).

The $\text{H}_3$ protons ($H_3$) of the guest experienced large upfield shifts. This indicates that the methyl protons point inside the hydrophobic aromatic cavity.$^{14}$

In conclusion, we have constructed a bowl-shaped superstructure 2a (or 2b) as the co-product by intra-clipping of resorcin[4]arene-based ligand 1a (or 1b) with square planar Pd(II) ions in water. The binding phenomena of aromatic carboxylates were demonstrated by ITC as well as by $^1$H NMR spectroscopy. The complexation processes are both enthalpically and entropically favoured in all cases.

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**Notes and references**


9. When ligand 1b and two equivalents of (en)Pd(NO$_3$)$_2$ were mixed in CDCl$_3$–CD$_2$OD = 10:1 (v/v) solution, oligomeric species were formed.

10. The change of a solvent system may cause variation in the donor ability of solvent molecules and/or in the solubility of charged molecules.

11. Upon complexation with Pd(II) ions, the pyridyl protons of the upper rim and the methyl protons of the lower rim become desymmetrized and appear as a pair of doublets. This also indicates the formation of rigid and $C_{3v}$ symmetric superstructures.

12. CSI-MS spectra of an aqueous solution of 1:2 mixture of 1a (or 1b) and (en)Pd(NO$_3$)$_2$ showed additional peaks which correspond to the inter-clipped supermolecular capsule 2a (or 3b), although we could not observe the existence of the dimeric capsule with NMR spectroscopy in D$_2$O. When performing the CSI-MS, 25% methanol and 2% DMF were added to the sample to solubilise it as well as for the enforcement of the ionisation strength. This is a possible explanation for the generation of the inter-clipped supermolecular capsule.


14. A relatively minute downfield shift for $H_3$ and a small upfield shift for the guest of 2a were also observed.