Molecular Engineering. Part 14. Self-Assembled Oligovelcraplexes
by \( \pi-\pi \) Stacking Interaction and Metal Coordination

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Various interesting supramolecular systems which self-assemble by noncovalent interactions have been developed rapidly. Cram et al. reported velcraplex which dimerize to velcraplex by solvophobic \( \pi-\pi \) stacking interactions.\(^1\) Based on this concept bisvelcrand composed of two velrand units bridged in back-to-back fashion by covalent bond was reported to self-assemble oligovelcraplex only by solvophobic \( \pi-\pi \) stacking interactions.\(^2\) Dalcanale et al. reported a dynamic velcraplex operating in multimodal fashions, solvophobic \( \pi-\pi \) stacking interaction of velcraplex unit and metal coordination of pyridyl feet, which is quite insoluble in normal organic solvents due to the freeze of all 4 feet by metal coordination.\(^3\)

New velcraplexes 1 and 2 composed of a 2-methylresorcinolarene-based quinoline kate velrand unit and a p-pyridylphenyl foot (Scheme 1), which are quite soluble in many organic solvents, were reported to form a dimer (bisvelcrand) by metal coordination.\(^4\) The characteristics of their self-assembled oligomeric nanostructures by solvophobic \( \pi-\pi \) stacking interaction and metal coordination were studied.

Scheme 1 shows the structural possibilities of self-assembled nanostructures based on velrand 1 or 2 which dimerize to bisvelcrand upon metal-coordination and then oligomerize to a linear or cyclic structure depending on the pyridyl unit and metal geometry. For example, velcraplex 1 and trans-Pd(DMSO)Cl\(_2\) will form Pd(II)-coordinated bisvelcrand 3, but velcraplex 1 and cis-Pt(dppp)(CF\(_3\)SO\(_2\))\(_2\) will form Pt(II)-coordinated bisvelcrand 4 as shown in Scheme 2. It is probable that bisvelcrands 3 and 4 may form a linear and a cyclic oligovelcraplexes, respectively.

MALDI-TOF mass spectra of 1 and 2 in CH\(_2\)Cl\(_2\) show molecular ion peaks at \( m/z \) 2825 attributable to velcraplexes [1\,4]\(^1\) or [2\,2]. Velcraplex 1\,4 and oligovelcraplex 3\(_n\) were observed by \( ^1\)H NMR spectroscopy. The \( ^1\)H NMR spectrum of velcraplex 1\,1 in CDCl\(_3\) (4.80 mM) at 298 K showed two kinds of methyl peaks (\( \delta \) 3.20 for out, \( \delta \) 2.31 for up as designated in Scheme 1) and three kinds of methine peaks (\( \delta \) 5.26, 3.61, 3.49 ppm). As this solution is diluted from 4.80 mM to 0.30, and then to 0.15 mM, methyl peaks for monomeric velcraplex 1 appeared at 2.70 ppm (for out methyl) and 2.50 ppm (for up methyl). These chemical shifts at high concentration (0.50 ppm down-field shift for out methyl, 0.19 ppm up-field shift for up methyl) prove the formation of velcraplex 1\,1 in solution.\(^7\) In case of oligovelcraplex 3\(_n\), in CDCl\(_3\) (4.80 mM) at 298 K appeared two kinds of methyl peaks (\( \delta \) 3.15 for out, \( \delta \) 2.26 for up) and three kinds of methine peaks (\( \delta \) 5.30, 3.56, 3.45 ppm). As this solution is diluted from 4.80 mM to 0.15 mM, methyl peaks for bisvelcrand 5 appeared at 2.60 (for out methyl) and 2.51 (for up methyl) ppm, which resulted in 0.55 ppm down-field shift for out methyl and 0.25 ppm up-field shift for up methyl upon oligovelcraplex formation in solution. The larger chemical shifts of oligobilvelcraplex 3\(_n\) compared to those of velcraplex 1\,1 (0.55 vs. 0.50 and 0.25 vs. 0.19) imply the stronger association of 3 than 1.

Square planar trans Pd(DMSO)Cl\(_2\) was prepared by the reaction of the PdCl\(_2\) with DMSO. Square planar cis bis(triflate) Pt(II) complex was prepared by the reaction of dppp (dppp = 1,3-bis diphenylphosphino)phane) and PtCl\(_2\), followed by exchange of the anionic ligands with AgOTf (OTf = triflate).\(^5\) Metal-coordinated 3 or 4 was formed by simply mixing velcraplex 1 with Pd(DMSO)Cl\(_2\) or Pt(dppp)(OTf) in a 2:1 molar ratio at room temperature in a nonpolar solvent such as CHCl\(_3\), CH\(_2\)Cl\(_2\).
The formation of oligobisvelcraplex 4, which is likely to be a cyclic tetramer \((m = 1)\) as shown in Scheme 1 was observed by the electrospray ionization mass spectrometry (ESI-MS), wherein the specific molecular ion peaks of tetrameric oligobisvelcraplex 4, were observed at \(m/z 1716.1\) \([(\text{1-Pd(dppp)OTf}_2-1)_4\text{-8OTf}]^8+\) (100\%, calc 1716.4), \(2338.1\) \([(\text{1-Pd(dppp)OTf}_2-1)_4\text{-6OTf}]^6+\) (20\%, calc 2338.2), and \(2835.8\) \([(\text{1-Pd(dppp)OTf}_2-1)_4\text{-5OTf}]^5+\) (10\%, calc 2835.8) as shown in Figure 1.

The energy barriers for pseudorotation between the so-called two kite conformers of velcraplexes 1, 2, 3, and 4 in high concentration were observed by VT \(^1^H\) NMR experiment\(^{5}\) in tetrachloroethane-d\(_2\) (Figure 2) and the results were summarized on Table 1. The chemical shifts of methyls of oligobisvelcraplex 3 and 4, in C\(_2\)D\(_2\)Cl\(_4\) were broadened and coalesced at about 130 °C and 120 °C to provide \(\Delta G^\circ\) of 18.5 kcal mol\(^{-1}\) and 18.0 kcal mol\(^{-1}\), respectively. But the corresponding coalescence temperatures for velcraplexes 1-1 and 2-2 were observed at 110 °C to give \(\Delta G^\circ\) of 17.5 kcal mol\(^{-1}\). The higher energy barrier for oligobisvelcraplexes 3 and 4, compared to those of velcraplexes 1-1 and 2-2 implies the higher steric hindrance imposed on 3 and 4 by extended association.

The pulsed-field gradient spin-echo (PGSE) NMR technique\(^{7}\) was used to measure the diffusion coefficients of CDCl\(_3\) solution of oligovelcraplex of 1-1 (oligobisvelcraplex 4,\(_p\)) and oligovelcraplex of 2-2 coordinated by Pt(II)(dppp) at

\[\text{Figure 1. Partial ESI-MS spectrum of Pt(II)-coordinated bisvelcraplex 4.}\]

\[\text{Figure 2. Variable temperature } ^1\text{H NMR spectra (400 MHz, CDCl}_3\text{)}\text{ of a) 1 at 298 K, b) 1 at 383 K, c) 4 at 298 K, and d) 4 at 393 K. }^{\ast}\text{: residual CHCl}_3\text{CHCl}_3\]
Table 1. The enolization temperatures and the activation energy barriers for pseudorotation between the two kite conformers of velcraplexes (400 MHz NMR in CDCl₃. The estimated error: ±0.5 kcal mol⁻¹)

<table>
<thead>
<tr>
<th>Velcraplex or</th>
<th>M(II)(L₂)</th>
<th>T enolization</th>
<th>ΔG°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligovelcraplex</td>
<td></td>
<td>K</td>
<td>kcal mol⁻¹</td>
</tr>
<tr>
<td>1:1</td>
<td>–</td>
<td>383</td>
<td>17.5</td>
</tr>
<tr>
<td>2:2</td>
<td>–</td>
<td>383</td>
<td>17.5</td>
</tr>
<tr>
<td>3₂</td>
<td>Pd(DMSO):Cl₂</td>
<td>403</td>
<td>18.5</td>
</tr>
<tr>
<td>4₄</td>
<td>Pd(dppp):OTf</td>
<td>393</td>
<td>18.0</td>
</tr>
</tbody>
</table>

298 K.

The measured diffusion coefficients show a noticeable change depending on the concentrations from 1.5 mM to 11.7 mM as shown in Figure 3. The concentration dependent decreases of diffusion coefficients indicate that metal-coordinated velcraplexes form larger self-assembly as its concentration increases. Overall the volume of oligovelcraplex of 2:2 increases faster than that of oligovelcraplex of 1:1. As proposed from the ESI mass spectral data, the relatively small volume change of oligovelcraplex of 1:1 (oligobisvelcraplex 4₄) as concentration increases may be also due to the formation of tetrameric cyclic structure shown in Scheme 1.

In conclusion, the formations of metal-coordinated oligobisvelcraplex were studied by ¹H NMR peak shifts comparison, the comparison of energy barrier for pseudorotation of kite conformers, and ESI MS. The pulsed-field gradient spin-echo (PGSE) NMR technique showed the volume change of oligovelcraplexes coordinated by Pt(II)-(dppp) depends on the position of nitrogen at pyridyl foot.

Experimental Section

Solvents and all commercially available reagents were used without any purification. All reactions were performed under argon. MALDI-TOF mass spectra were run on a Voyager-DE STR Biospectrometry. Electrospray ionization (ESI)-MS experiments were performed on a Micromass QTOF2-MS spectrometer (Korea Basic Science Institute). ¹H NMR spectra were recorded on a Bruker Avance (400 MHz).

Pulsed field gradient spin-echo (PGSE) NMR experiments. The diffusion coefficient measurements were carried out using a 5 mm Bruker QNP probe with an actively shielded gradient coil. Diffusion coefficients were extracted from a series of ¹H NMR spectra measured by the bipolar pulse longitudinal encode-decode (BIPLED) pulse sequence as a function of gradient amplitude. In each experiment, the gradient duration time was 2.0 or 2.5 ms and the amplitude of gradient pulses ranged from 1 to 40 G/cm. The diffusion time was 50 to 100 ms. Diffusion coefficients were calculated from the data obtained by 2D diffusion-ordered spectroscopy (DOSY).

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References