Molecular Engineering. Part 14. Self-Assembled Oligovelcraplexes by π-π 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 velcrand which dimerize to velcraplex by solvophobic π-π stacking interactions.[1] Based on this concept bisvelcrand composed of two velcrand units bridged in back-to-back fashion by covalent bond was reported to self-assemble oligovelcraplex only by solvophobic π-π stacking interactions.[2] Dalcanale *et al.* reported a dynamic velcrand operating in multimodal fashions, solvophobic π-π stacking interaction of velcrand 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 velcrands **1** and **2** composed of a 2-methylresorcin-[4]arene-based quinoxaline kite velcrand 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 π-π stacking interaction and metal coordination were studied.

Scheme 1 shows the structural possibilities of self-assembled nanostructures based on velcrand **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, velcrand **1** and *trans*-Pd(DMSO)$_2$Cl$_2$ will form Pd(II)-coordinated bisvelcrand **3**, but velcrand **1** and *cis*-Pt(dppp)(CF$_3$SO$_3$)$_2$ 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 [1·1]$^+$ or [2·2]$^-$. Velcraplex 1·1 and oligobisvelcraplex **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 (δ3.20 for out, δ2.31 for up as designated in Scheme 1) and three kinds of methine peaks (δ 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 velcrand **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 methyls) prove the formation of velcraplex 1·1 in solution.[5] In case of oligobis-

1. R = CH$_2$(CH$_2$)$_3$CH , R'-

2. R = CH$_2$(CH$_2$)$_3$CH . R'-
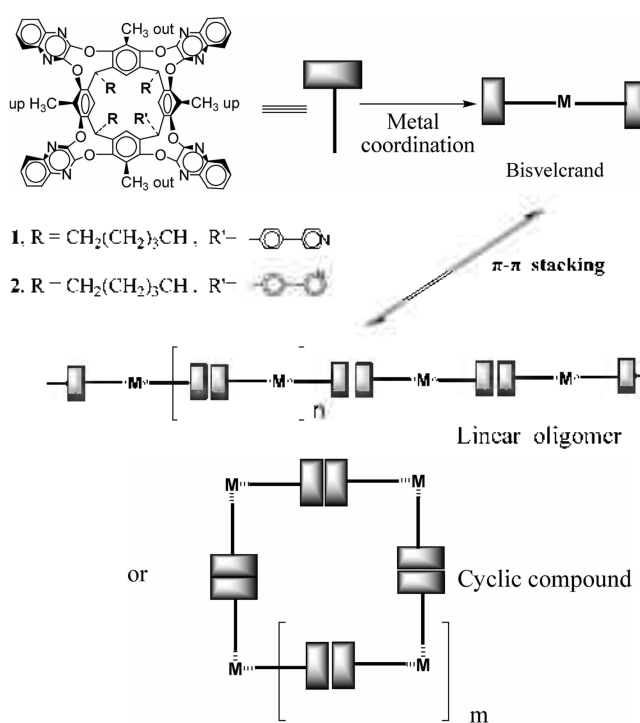
Scheme 1

velcraplex **3**$_n$ in CDCl$_3$ (4.80 mM) at 298 K appeared two kinds of methyl peaks (δ 3.15 for out, δ 2.26 for up) and three kinds of methine peaks (δ 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 methyls upon oligovelcraplex formation in solution. The larger chemical shifts of oligobisvelcraplex **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)$_2$Cl$_2$ was prepared by the reaction of the PdCl$_2$ with DMSO. Sqaure planar *cis* bis(triflate) Pt(II) complex was prepared by the reaction of dppp (dppp = 1,3-bis diphenylphosphinoprophane) and PtCl$_2$, followed by exchange of the anionic ligands with AgOTf (OTf = triflate).[6] Metal-coordinated **3** or **4** was formed by simply mixing velcrand **1** with Pd(DMSO)$_2$Cl$_2$ or Pt(dppp)(OTf)$_2$ in a 2:1 molar ratio at room temperature in a nonpolar solvent such as CHCl$_3$, CH$_2$Cl$_2$.
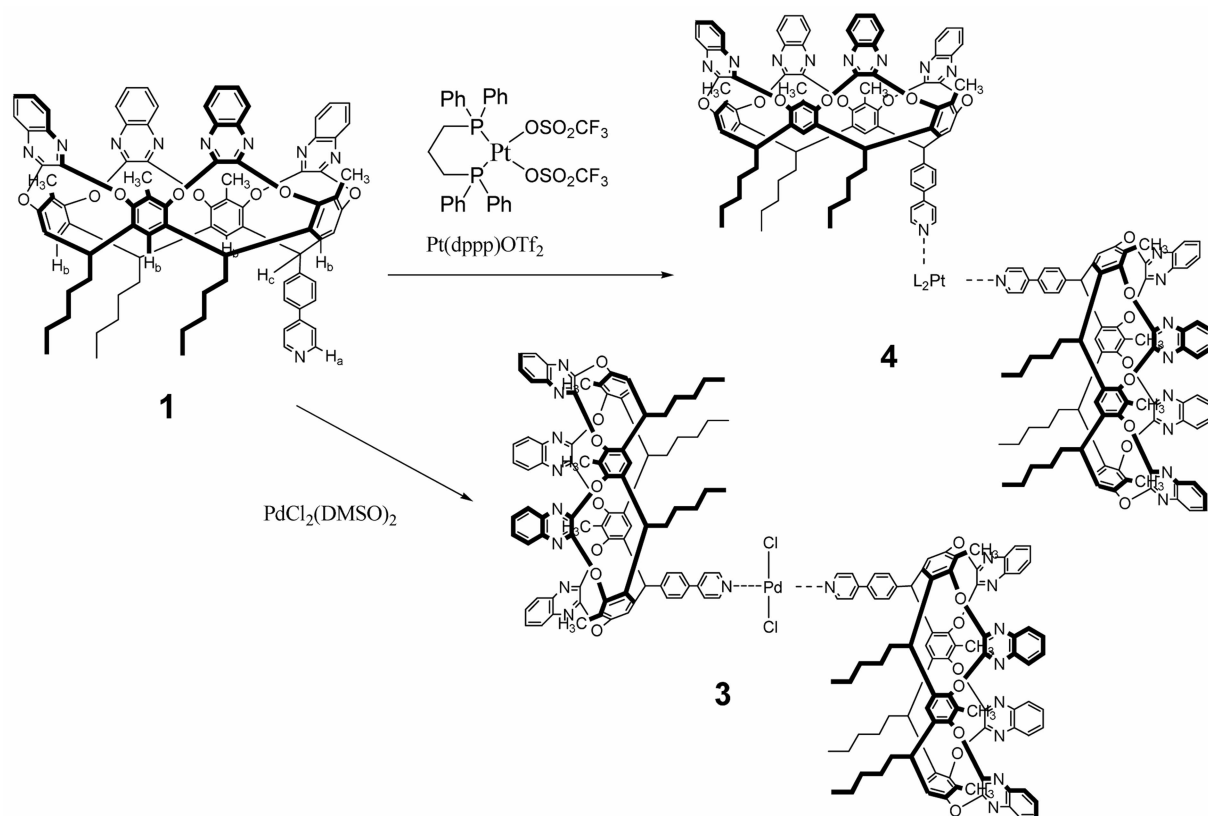
Scheme 2

The formation of oligobisvelcraplex 4_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_4 were observed at m/z 1716.1 [(1-Pd(dppp)OTf$_2$-1)$_4$-8OTf]$^{8+}$ (100%, calc 1716.4), 2338.1 [(1-Pd(dppp)OTf$_2$-1)$_4$-6OTf]$^{6+}$ (20%, calc 2338.2), and 2835.8 [(1-Pd(dppp)OTf$_2$-1)$_4$-5OTf]$^{5+}$ (10%, calc 2835.8) as shown in Figure 1.

The energy barriers for pseudorotation between the so-called two kite confomers 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_n and 4_n in C$_2$D$_2$Cl$_4$ were broadened and coalesced at about 130 °C and 120 °C to provide $\Delta G^\ddagger$ 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 $\Delta G^\ddagger$ of 17.5 kcal mol^{-1}. The higher energy barrier for oligbisvelcraplexes 3_n and 4_n 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_n) and oligovelcraplex of 2·2 coordinated by Pt(II)(dppp) at
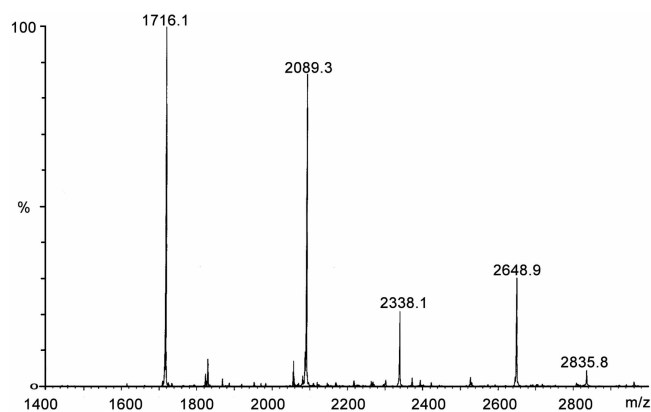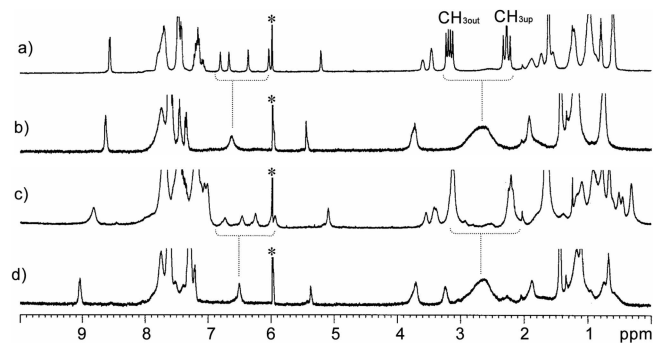
Table 1. The coalescence temperatures and the activation energy barriers for pseudorotation between the two kite conformers of velcrands (400 MHz NMR in $C_2D_2Cl_4$. The estimated error: ± 0.5 kcal mol^{-1})

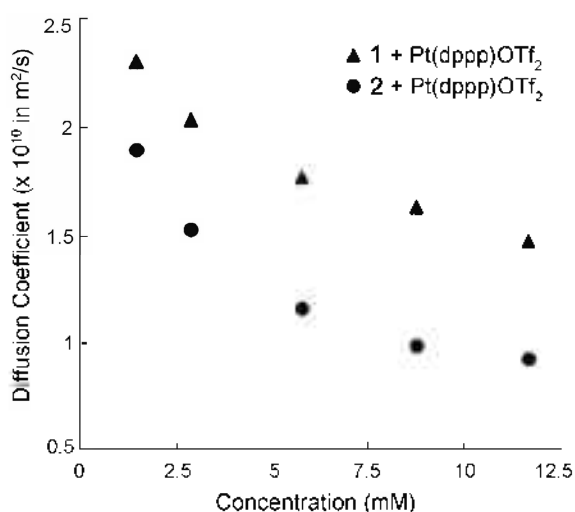| Velcraplex or Oligovelcraplex	M(II)(L$_2$)	T$_{coalescence}$, K	$\Delta G^{\ddagger}$, kcal mol^{-1}
1·1	–	383	17.5
2·2	–	383	17.5
3$_n$	Pd(DMSO)$_2$Cl$_2$	403	18.5
4$_n$	Pt(dppp)OTf$_2$	393	18.0

Figure 3. Concentration dependences of diffusion coefficients of oligovelcraplexes of 1·1 and 2·2 coordinated by Pt(II)(dppp) in CDCl$_3$ at 298 K.

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 4$_n$) as concentration increases may be also due to the formation of tetrameric cyclic structure shown in Scheme 1.

In conclusion, the formations of their metal-coordinated oligobisvelcraplex were studied by ^{1}H 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). ^{1}H NMR spectra were recorded on a Brucker 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 z gradient coil. Diffusion coefficients were extracted from a series of ^{1}H NMR spectra measured by the bipolar pulse longitudinal encode-decode (BPPLED) pulse sequence as a function of gradient amplitude. In each experiment, the gradient duration time was 2.0 or 2.5 ms and the amplitudes 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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