<table>
<thead>
<tr>
<th>Title</th>
<th>Reversible formation and cleavage of Pt→Ag dative bonds in a pre-organized cavity of a luminescent heteropolynuclear platinum(ii) complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Ueda, Misa; Horiuchi, Shinnosuke; Sakuda, Eri; Nakao, Yoshihide; Arikawa, Yasuhiro; Umakoshi, Keisuke</td>
</tr>
<tr>
<td>Citation</td>
<td>Chemical Communications, 53(48), pp.6405-6408; 2017</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2017-06-18</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10069/37698">http://hdl.handle.net/10069/37698</a></td>
</tr>
<tr>
<td>Right</td>
<td>© The Royal Society of Chemistry 2017</td>
</tr>
</tbody>
</table>
U-shaped Pt$_2$Ag$_2$, complex [Pt$_2$Ag$_3$(ppy)$_2$(Ph$_2$pz)$_4$] with pre-organized cavity (ppy = 2-phenylpridinate, Ph$_2$pz = 3,5-diphenylpyrazolato) and related complexes have been prepared. The Pt$_2$Ag$_2$ complexes react with Ag(I) ion to give corresponding Pt$_2$Ag$_3$ complexes accompanying Pt→Ag dative bonds. It became obvious that the existence of C(ipso) atom in the chelate ligand is important as the driving force for forming Pt→Ag dative bonds. However, once the Pt$_2$Ag$_3$ complex is formed, the trapped Ag(I) ion is mainly stabilized by the Pt→Ag dative bonds, which are stronger than the Ag-C(ipso) bond. The trapped Ag(I) ion can be abstracted from the cavity selectively by adding an equivalent amount of chloride ion into the solution of Pt$_2$Ag$_3$ complexes to reproduce original Pt$_2$Ag$_2$ complexes.

Guest recognitions as inspired enzymatic behavior are often observed via reversible bond formation and noncovalent interactions. Generally, hydrogen bonds, several interactions such as electrostatic, aromatic π-π, charge-transfer, and cation-π, and hydrophobic effect play important roles to construct host-guest supramolecular structures, which show attractive phenomena that are unobservable from each component. Recently, supramolecular systems based on metal–metal interactions exhibited interesting UV-Vis absorption and emission changes upon host-guest association. These results led us to a new design of supramolecular system based on heteropolynuclear transition-metal complexes. Heteropolynuclear complexes are expected to exhibit characteristic interactions and cooperative effects between the transition elements, providing novel functions that are unobtainable through the individual element.

Metal-metal dative bonds (Pt→M dative bonds) are known to exhibit significant metal-metal interactions between heterometal atoms in the solid state. Although the Pt→M dative bonds are observed in various kinds of heteropolynuclear complexes, one of the most popular dative bonds is the Pt→Ag dative bond. For example, it is known that the reactions of anionic mononuclear Pt(II) complexes bearing cyclometalated benzquinolinate and two pentahalophenyl ligands with Ag(I) ion afford heteropolynuclear complexes with Pt→Ag dative bonds. However, it is likely that the heteropolynuclear complexes accompanying Pt→Ag dative bonds formed by the reaction of mononuclear precursor complex (or complex ion) with Ag(I) ion are less stable in solution, owing to the labile nature of Pt→Ag dative bonds. This is in contrast to the Pt-Au complex accompanying Pt→Au dative bond, which is more stable in solution without supporting bridging ligands. Since the reactivity and photophysical properties of Pt-Ag complexes accompanying Pt→Ag dative bond are not fully understood, it is important to construct the system stable in solution for elucidating the nature of Pt→Ag dative bond. Thus we intended to apply the Pt→Ag dative bond for constructing new supramolecular system based on a heteropolynuclear framework. This system will not only allow us to study the nature of Pt→Ag dative bond in solution, but endow us with some insights to establish new supramolecular systems.

We have previously reported that the reaction of mononuclear Pt(II) complexes bearing C=N chelate ligands (C=N = ppy, dipp, bzx; dipp = 2-(2,4-difluorophenyl)pyridinate) and Me$_2$pzH (Me$_2$pzH = 3,5-dimethylpyrazole) with Ag(I) ion potently afford both of the Z-shaped and U-shaped Pt$_2$Ag$_3$ complexes, though either of the two geometrical isomers was found as the solid state structure.
of each complex. Recently, we also established new types of emissive supramolecular system via molecular recognition by using hydrogen-bonded capsule and emissive Ir(III) complexes.  It is expected that steric hindrance from bulky bridging ligand such as Ph2pz (Ph2pzH = 3,5-diphenylpyrazole) selectively gives U-shaped Pt2Ag3 complexes having a binding pocket for metal ions via multiple metal-metal interactions in the framework. Since the pre-organized structures of heteropolynuclear complexes are stable in solution, these heteropolynuclear complexes are ideal and epoch-making system for studying the nature of dative bonds in solution.  Herein, we report the heteropolynuclear complex, which can reversibly capture Ag(I) ion into and release it from the pre-organized cavity by the concerted formation and cleavage of Pt→Ag dative bonds and Ag-C(ipso) bonds, respectively, as well as new insights into the nature of dative bond.

The reaction of di(μ-chloro) Pt(II) dimer [Pt2(ppy)2(μ-Cl)2] with Ph2pzH afforded a mononuclear complex [Pt(ppy)(Ph2pzH)]Cl (1a). The neutral U-shaped Pt2Ag2 complex [Pt2Ag2(ppy)2(Ph2pz)] (2a) and cationic Pt2Ag3 complex [Pt2Ag3(ppy)2(Ph2pz)]BF4 (3a) were selectively obtained by the reaction of 1a with Ag(I) ion in the presence of Et3N by controlling the amount of Ag(I) ion and the volume of reaction solvent (Scheme 1). The reaction of 2a with AgBF4 also gave 3a. In addition, the Me2pz analogue of Pt2Ag3 complex [Pt2Ag3(ppy)(Me2pzH)]BF4 (3b) was obtained in a similar manner. The structures of 2a and 3a were revealed by single crystal X-ray structural analyses.

The structures of 2a and cationic part of 3a are shown in Fig. 1 along with a selection of relevant bond distances. Distinct from the Me2pz-bridged Pt2Ag2 complex 2b having Z-shaped structure in the solid state, the Ph2pz-bridged Pt2Ag3 complex 2a has U-shaped structure both in the solid state and in solution as revealed by 1H NMR spectroscopy (see below). The view along Pt1Pt2Pt axis of 2a shows that the pyridine rings in each ppy ligand take eclipsed configuration (Fig. 1). The Pt1Pt2Ag3 (3.2028(3), 3.4249(3) Å) and Ag1Ag distances (3.063(1) Å) in 2a are comparable to those in Me2pz analogue 2b (Pt1Pt2Ag3: 3.2815(7), 3.4301(8) Å; Ag1Ag: 3.1772(7) Å). The complex 2a exhibits simple 1H NMR spectrum implying the existence of single geometrical isomer in solution at 296 K (Fig. 2) and Z-shaped structure seems to be less stable than U-shaped structure owing to the steric hindrance of bulky substituent groups on the bridging pyrazolate ligands, the appearance of small resonances in the 1H NMR spectra at low temperature indicates the existence of other geometrical isomers as minor species (Fig. S7). The possible geometrical isomers are also shown in Fig. S7.

On the contrary, the phenyl rings in each ppy ligand take approximately eclipsed configuration in the Pt2Ag3 complex 3a. It is obvious from the view along Pt1Pt2Pt axis in 3a that the additional Ag(I) ion is sandwiched between Pt1-C122 and Pt2-C422 bonds (Fig. 1). The short Ag3Ag3 (2.41(1) Å) and Ag3Ag3 (2.48(1) Å) distances indicate the formation of Ag-C(ipso) bonds. Furthermore, the Pt1Ag1Ag3 (2.80(1) Å) and Pt2Ag1Ag3 (2.80(1) Å) distances are ca. 0.5 Å shorter than the other PtAgAg distances in 3a defined by Pt1, Pt2, Ag1 and Ag2 atoms (3.01(1)–3.44(1) Å), indicating the formation of strong Pt→Ag dative bonds. The Pt1Ag3 distances for dative bond in 3a are comparable to those in a chain complex [Pt(ppy)2{Ag(acetone)}3]2+ (2.6781(9)–2.8121(9) Å). The Ag1Ag3 (2.996(1) Å) and Ag2Ag3 (3.063(1) Å) distances are shorter than the Ag1AgAg2 distance (3.22(1) Å), implying that the incorporated Ag(I) ion is additionally stabilized by the Ag@Ag contacts. The complex 3a gave a slightly broadened simple 1H NMR spectrum, which shows the existence of single geometrical isomer in solution. The variable-temperature 1H NMR spectra of 3a, which exhibit no splitting of resonances with
Pt₂Ag₂ and Pt₂Ag₃ complexes, abstracted by the addition of an equivalent amount of dative bonds and Ag-C(ipso) bonds in Pt₂Ag₃ complex, which was revealed by 1H NMR spectroscopy as abstracted by the addition of an equivalent amount of –3073 and –2576 ppm (vs H₂PtCl₆ in D₂O in CH₂Cl₂/CDCl₃), the 195Pt NMR signal of

well (Fig. S8). Similar behavior towards chloride ion was observed ion. However, the incorporation of Ag(I) ion was not observed for a Pt₂Ag₃ complex

3b

This observation clearly indicates that the Pt→Ag dative bond in solution, we measured 195Pt NMR spectra of

bond.

X-ray structural analysis. Variable-temperature 1H NMR spectra of

reproduce

very interestingly, the Ag(I) ion forming Pt₂Ag3 complex is formed, the trapped Ag ion is mainly stabilized C(ipso) bond and Ag

interaction observed in the heteropolynuclear complexes accompanying Pt→Ag dative bond.

The Pt₂Ag₂ and Pt₂Ag₃ complexes exhibit bright yellow-green emission with high quantum yields in the solid state irrespective of bridging ligands (Φ = 0.17 (2a), 0.34 (2b),0.15 (3a), 0.53 (3b); Table S3). However, the features of the emission spectra of Pt₂Ag₃ complexes are different from those of Pt₂Ag₂ complexes; the former complexes 2a and 2b exhibit structure and dative bond.

It was found that the reaction of Z-shaped Me₅pz-bridged Pt₂Ag₂ complex 2b with an equivalent amount of Ag(I) ion also affords a Pt₂Ag₃ complex 3b, which was confirmed by elemental analysis, ESI-MS, 1H NMR spectroscopy (Figs. S4 and S5) and preliminary X-ray structural analysis. Variable-temperature 1H NMR spectra of 3b further suggest the existence of single geometrical isomer in solution (Fig. S6). Similarly to 3a, the Ag(I) ion forming Pt→Ag dative bonds and Ag-C(ipso) bonds in 3b can be selectively abstracted by the addition of an equivalent amount of n-BuNCl, which was confirmed by the 1H NMR spectrum of the reaction product obtained by the treatment of 3a with n-BuNCl (Fig. 2). This observation clearly indicates that the Pt→Ag dative bond is weaker than the Ag-Npyrazolate bond in spite of the existence of additional support by Ag-C(ipso) bond.

The absorption bands of Pt₂Ag₂ complex 2a and cationic parts of Pt₂Ag₃ complexes (3a' and 3b') were theoretically investigated with the time-dependent density functional theory (TD-DFT) method. Calculated transition energies agree well with the experimental results (Tables S10–S12). The molecular orbitals, which contribute to the excitations in Tables S10–S12, are depicted in Figs. S15–S18. Orbital composition percentages of these orbitals are listed in Table S13. Upon optimizing the geometry of excited triplet state, two stable geometries were found for 3b': the geometry of T₁₉ is ca. 1.0 kcal/mol more stable than that of T₁₆ (Fig. S18).

The Mayer bond indices computed for Ag-C(ipso) bonds (0.18 (3a'), 0.18 (3b')) in Pt₂Ag₂ complex (0.32 (3a'), 0.32 (3b')) and Ag@@Ag contacts (0.11 (3a'), 0.10 (3b')) suggest that the strength of the Pt→Ag dative bond is significantly higher than those of Ag-C(ipso) bond and Ag@@Ag contact. It indicates that, once the Pt₂Ag₂ complex is formed, the trapped Ag ion is mainly stabilized by the Pt→Ag dative bonds, though the existence of C(ipso) atom is important as the driving force for forming Pt→Ag dative bonds (Table S4). Furthermore, it was disclosed that the Mayer bond indices in the excited triplet states computed for the Pt→Ag dative bonds (0.22 (3a'), 0.21 (3b')) and the Ag-C(ipso) bonds (0.11 (3a'), 0.07 (3b')) decreased with increase of those for Ag@@Ag contacts (0.23 (3a'), 0.22 (3b')).

The absorption bands of Pt₂Ag₂ complex 2a and cationic parts of Pt₂Ag₃ complexes (3a' and 3b') were calculated by the TD-DFT method. The lowest energy absorption bands of Pt₂Ag₂ complex (2a) can be assigned mainly to the combination of the ligand-to-ligand charge-transfer (LLCT) [Ph₃pz–π*(ppy)] and metal-to-ligand charge-transfer (MLCT) [Pt→π*(ppy)] transitions, while those of Pt₂Ag₃ complexes (3a, 3b) can be mainly assigned to the charge transition transition from Ph₃pz bridging ligand to Pt₃Ag₃(ppy) moiety, LMM'LLCT [Ph₃pz→PtAg/π*(ppy)] transition. Optimization of the geometries of triplet excited states revealed that, similarly to the previously reported emission of 2b,0.30 that of 2a can also be attributed to phosphorescence mainly from 3LC [π–π*(ppy)] excited state. On the other hand, the emissions of 3a and 3b can be attributed to phosphorescence mainly from 3LMM'L'CT [Ph₃pz→PtAg/π*(ppy)] excited state. These assignments are fully consistent with the observations that the Pt₂Ag₂ complexes exhibit
structured emission spectra, while the Pt-Ag₃ complexes exhibit broad ones.

In conclusion, metal-metal dative bond was focused for developing functional molecules based on non-covalent bonding interactions. We have succeeded in the synthesis of U-shaped Pt-Ag₃ complex [Pt₂Ag₃(tpy)(Phpza)] having pre-organized cavity suitable for incorporating Ag(I) ion. The Ag(I) ion trapped in the cavity was stabilized by the Pt→Ag dative bonds which are stronger than the Ag-C(ipso) bond. Furthermore, the trapped Ag(I) ion could be abstracted from the cavity selectively by adding an equivalent amount of chloride ion into the solution of Pt-Ag₃ complex. The formation of Pt→Ag dative bonds drastically changes the structured emission spectrum into broad one with altering the emissive state from 1LC excited state to 2LMM'LCT excited state. Consequently, a reversible formation and cleavage of Pt→Ag dative bonds within the pre-organized cavity of Pt-Ag₃ complex has successfully been demonstrated. ELudication of the properties of ground and excited states added new insights into the nature of dative bond.

This work was partially supported by JSPS KAKENHI Grant Number 15K05456, 17K14463 and Nippon Sheet Glass Foundation for Materials Science and Engineering.

Notes and references
7 The ¹H NMR spectrum of a 1:1 mixture of 2a and 3a recorded at room temperature was merely a superposition of the spectra of 2a and 3a and showed no coalescence of signals. It indicates that dissociation of the third Ag⁺ ion from the cavity and the exchange reaction of Ag⁺ ion do not proceed at least in the NMR timescale (Fig. S10).