

Reversible Formation and Cleavage of Pt→Ag Dative Bonds in a Pre-organized Cavity of Luminescent Heteropolynuclear Platinum(II) Complex

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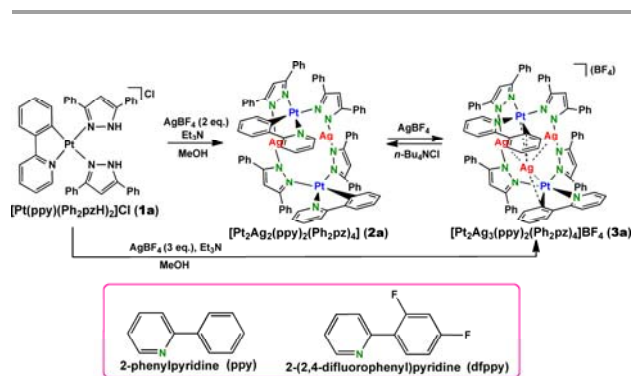
U-shaped Pt₂Ag₂ complex [Pt₂Ag₂(ppy)₂(Ph₂pz)₄] with pre-organized cavity (ppy = 2-phenylpyridinate, Ph₂pz = 3,5-diphenylpyrazolate) and related complexes have been prepared. The Pt₂Ag₂ complexes react with Ag(I) ion to give corresponding Pt₂Ag₃ complexes accompanying Pt→Ag dative bonds. It became obvious 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 Pt₂Ag₃ 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 Pt₂Ag₃ complexes to reproduce original Pt₂Ag₂ 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 interactions, and hydrophobic effect play important roles to construct host-guest supramolecular structures, which show attractive phenomena that are unobservable from each component.¹ Recently, supramolecular systems based on metal-metal interactions exhibited interesting UV-Vis absorption and emission changes upon host-guest association.² 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.³

Metal-metal dative bonds (Pt→M dative bonds) are known to exhibit significant metal-metal interactions between heterometal atoms in the solid state.^{3d, 4} 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 benzoquinolate and two pentahalophenyl ligands with Ag(I) ion afford heteropolynuclear complexes with Pt→Ag dative bonds.^{4e, 4g} 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.^{4k} Since the reactivity and photophysical properties of Pt-Ag complexes accompanying Pt→Ag dative bond are not fully understood,⁵ 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, dfppy, bzq; dfppy = 2-(2,4-difluorophenyl)pyridinate) and Me₂pzH (Me₂pzH = 3,5-dimethylpyrazole) with Ag(I) ion potentially afford both of the Z-shaped and U-shaped Pt₂Ag₂ complexes, though either of the two geometrical isomers was found as the solid state structure



Scheme 1 Synthesis of [Pt₂Ag₂(ppy)₂(Ph₂pz)₄] (**2a**) and [Pt₂Ag₃(ppy)₂(Ph₂pz)₄]BF₄ (**3a**) and C^N chelate ligands employed in this study.

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of each complex.^{3h} Recently, we also established new types of emissive supramolecular system via molecular recognition by using hydrogen-bonded capsule and emissive Ir(III) complexes.⁶ It is expected that steric hindrance from bulky bridging ligand such as Ph₂pz (Ph₂pzH = 3,5-diphenylpyrazole) selectively gives U-shaped Pt₂Ag₂ 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]⁷ with Ph₂pzH afforded a mononuclear complex [Pt(ppy)(Ph₂pzH)₂Cl] (**1a**). The neutral U-shaped Pt₂Ag₂ complex [Pt₂Ag₂(ppy)₂(Ph₂pz)₄] (**2a**) and cationic Pt₂Ag₃ complex [Pt₂Ag₃(ppy)₂(Ph₂pz)₄]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)₂(Me₂pz)₄]BF₄ (**3b**) was obtained in a similar manner. The structures of **2a** and **3a** were revealed by single crystal X-ray structural analyses.

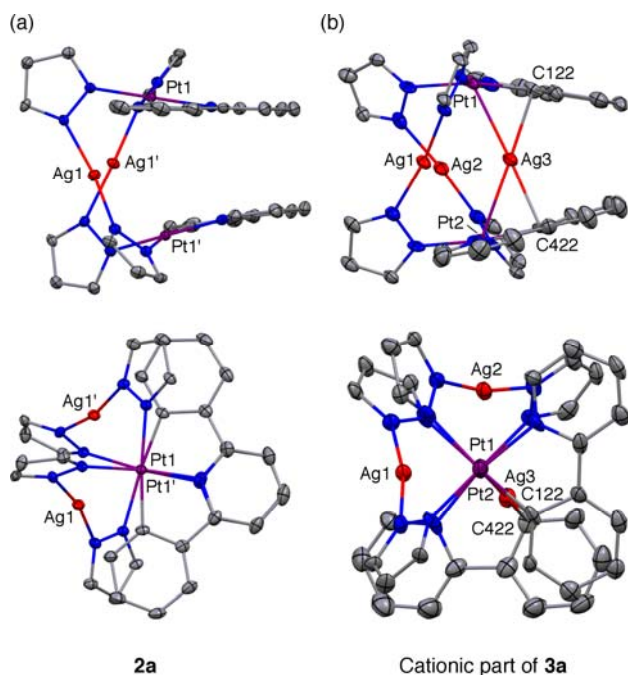


Fig. 1 ORTEP drawings of a) [Pt₂Ag₂(ppy)₂(Ph₂pz)₄] (**2a**) and b) cationic part of [Pt₂Ag₃(ppy)₂(Ph₂pz)₄]BF₄ (**3a**) with the atom numbering scheme (50% probability ellipsoids): (top) side view, (bottom) viewed along Pt⊕⊕Pt axis. Phenyl groups are omitted for clarity. Selected bond distances [Å] for **2a**: Pt1⊕⊕Pt1', 4.6707(4); Pt1⊕⊕Ag1, 3.2028(3); Pt1⊕⊕Ag1', 3.4249(3); Ag1⊕⊕Ag1', 2.9840(4). **3a**: Pt1⊕⊕Pt2, 5.1641(9); Pt1⊕⊕Ag1, 3.421(1); Pt1⊕⊕Ag2, 3.327(1); Pt1⊕⊕Ag3, 2.820(1); Pt2⊕⊕Ag1, 3.301(1); Pt2⊕⊕Ag2, 3.443(1); Pt2⊕⊕Ag3, 2.801(1); Ag1⊕⊕Ag2, 3.224(1); Ag1⊕⊕Ag3, 2.996(1); Ag2⊕⊕Ag3, 3.063(1); Ag1⊕⊕C122, 2.41(1); Ag3⊕⊕C422, 2.48(1).

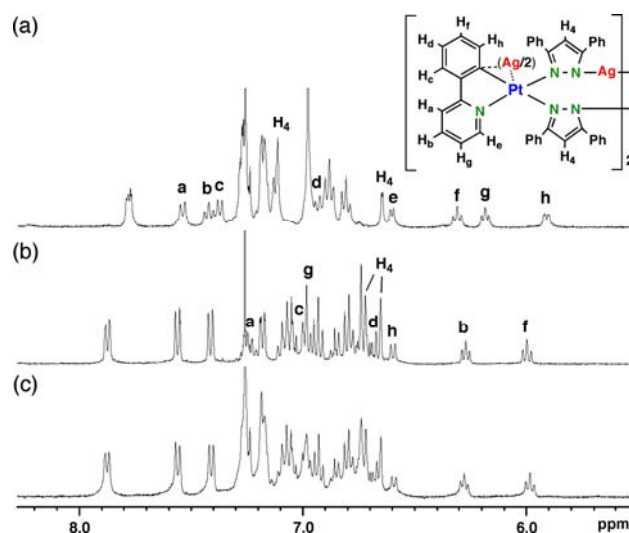


Fig. 2. ¹H NMR spectra (400 MHz, CDCl₃, 296 K) of a) [Pt₂Ag₃(ppy)₂(Ph₂pz)₄]BF₄ (**3a**), b) [Pt₂Ag₂(ppy)₂(Ph₂pz)₄] (**2a**) and c) reaction product obtained by the treatment of **3a** with Bu₄NI at 313 K.

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,^{3h} the Ph₂pz-bridged Pt₂Ag₂ 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 Pt⊕⊕Pt axis of **2a** shows that the pyridine rings in each ppy ligand take eclipsed configuration (Fig. 1). The Pt⊕⊕Ag (3.2028(3), 3.4249(3) Å) and Ag⊕⊕Ag distances (2.9840(4) Å) in **2a** are comparable to those in Me₂pz analogue **2b** (Pt⊕⊕Ag: 3.2815(7), 3.4301(8) Å; Ag⊕⊕Ag: 3.1772(7) Å).^{3h} Although **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 Pt⊕⊕Pt axis in **3a** that the additional Ag(I) ion is sandwiched between Pt1-C122 and Pt2-C422 bonds (Fig. 1). The short Ag3⊕⊕C122 (2.41(1) Å) and Ag3⊕⊕C422 (2.48(1) Å) contacts indicate the formation of Ag-C(ipso) bonds. Furthermore, the Pt1⊕⊕Ag3 (2.820(1) Å) and Pt2⊕⊕Ag3 (2.801(1) Å) distances are ca. 0.5 Å shorter than the other Pt⊕⊕Ag distances (3.301(1)–3.443(1) Å), indicating the formation of strong Pt→Ag dative bonds. The Pt⊕⊕Ag distances for dative bond in **3a** are comparable to those in a chain complex [{Pt(ppy)₂}{Ag(acetone)}₂]_n²ⁿ⁺ (2.6781(9)–2.8121(9) Å).^{4b} The Ag1⊕⊕Ag3 (2.996(1) Å) and Ag2⊕⊕Ag3 (3.063(1) Å) distances are shorter than the Ag1⊕⊕Ag2 distance (3.224(1) Å), implying that the incorporated Ag(I) ion is additionally stabilized by the Ag⊕⊕Ag contacts.⁸ 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

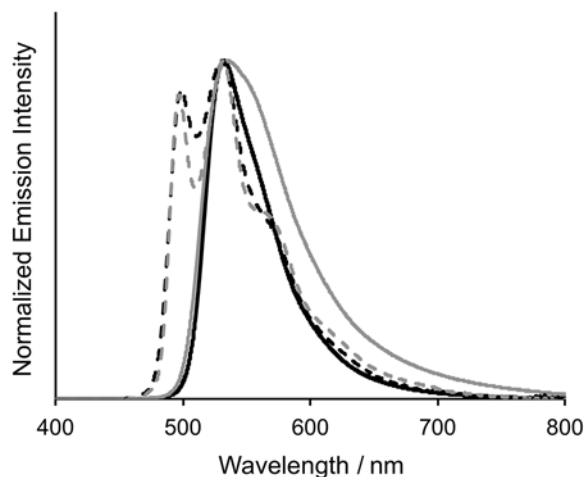


Fig. 3 Normalized emission spectra of **2a** (—), **2b** (---), **3a** (····) and **3b** (-·-·) in the solid state at 295 K ($\lambda_{\text{ex}} = 350$ nm). ^a Ref. 3h.

decreasing temperature, further confirmed it (Fig. S6). These observations can be attributed to the restricted rotation of Pt coordination planes along Pt^{⊕⊕⊕}Pt axis owing to the formation of Ag-C(ipso) bonds in **3a**. Very interestingly, the Ag(I) ion forming Pt→Ag dative bonds and Ag-C(ipso) bonds in **3a** can be selectively abstracted by the addition of an equivalent amount of *n*-Bu₄NCl, which was confirmed by the ¹H NMR spectrum of the reaction product obtained by the treatment of **3a** with *n*-Bu₄NCl (Fig. 2). This observation clearly indicates that the Pt→Ag dative bond is weaker than the Ag-N_{pyrazolate} bond in spite of the existence of additional support by Ag-C(ipso) bond.

It was found that the reaction of Z-shaped Me₂pz-bridged Pt₂Ag₂ complex **2b**^{3h} 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*-Bu₄NCl to reproduce **2b** (Fig. S4). In addition, the Ph₂pz-bridged dfppy analogue of Pt₂Ag₂ complex **5a** also reacts with Ag(I) ion to give Pt₂Ag₃ complex, which was revealed by ¹H NMR spectroscopy as well (Fig. S8). Similar behavior towards chloride ion was observed for the Pt₂Ag₃ complex produced by the reaction of **5a** with Ag(I) ion. However, the incorporation of Ag(I) ion was not observed for a U-shaped Me₂pz-bridged Pt₂Ag₂ complex bearing N[^]N chelate ligand [Pt₂Ag₂(bpy)₂(Me₂pz)₄](PF₆)₂ (Fig. S9).^{3h} These observations clearly indicate that the existence of C(ipso) atom in the chelate ligand is important as the driving force for forming Pt→Ag dative bond.

To obtain further evidence of the persistence of Pt→Ag dative bond in solution, we measured ¹⁹⁵Pt NMR spectra of **2a** and **3a**. The Pt₂Ag₂ and Pt₂Ag₃ complexes, **2a** and **3a**, showed sharp signals at -3073 and -2576 ppm (vs H₂PtCl₆ in D₂O in CH₂Cl₂/CDCl₃), respectively (Fig. S11). The large downfield shift ($\Delta = 497$ ppm) of the ¹⁹⁵Pt NMR signal of **3a** is a clear evidence for the presence of Pt→Ag dative bond: the downfield shift of **3a** is about two times larger than that of Pt₂Ag complex, [(EtOOC-

C[^]N[^]C)Pt(dmpyz)₂Ag]BF₄ ($\Delta = 250$ ppm)^{4h} and ca. 100 ppm larger than that of [Pt(phpy)₂] in the presence of excess amount of AgClO₄.^{4b} Furthermore, a sharp doublet signal was observed for **3a** with strong ¹⁹⁵Pt-^{107,109}Ag coupling ($^1J(^{195}\text{Pt}-^{107,109}\text{Ag}) = 766$ Hz) even at room temperature. This is sharp contrast to the ¹⁹⁵Pt NMR spectrum of [(EtOOC-C[^]N[^]C)Pt(dmpyz)₂Ag]BF₄ that a doublet signal ($^1J(^{195}\text{Pt}-^{107,109}\text{Ag}) = 455$ Hz) was observed only at lower temperature (193 K) due to the fast formation-dissociation equilibrium of Pt-Ag dative bond at room temperature.^{4h} Thus the ¹⁹⁵Pt NMR spectrum of **3a** undoubtedly indicates that additional Ag⁺ ion is strongly trapped in the cavity via multiple Pt-Ag and Ag-Ag interactions. To our knowledge, this is the strongest Pt-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 ($\Phi = 0.17$ (**2a**), 0.34 (**2b**),^{3h} 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**^{3h} exhibit structured emission spectra, while the latter complexes **3a** and **3b** exhibit broad ones (Fig. 3).

To shed light on the nature of Pt→Ag dative bond and Ag-C(ipso) bond in Pt₂Ag₃ complexes as well as on the photophysical properties of Pt₂Ag₂ and Pt₂Ag₃ complexes, the transition energies and oscillator strengths from singlet ground states for 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 T_{1a} is ca. 1.0 kcal/mol more stable in energy than that of T_{1b} (Fig. S18).

The Mayer bond indices computed for Ag-C(ipso) bonds (0.18 (**3a'**), 0.18 (**3b'**)), Pt→Ag dative bonds (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 Pt₂Ag₃ 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) [Ph₂pz→ 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 transfer transition from Ph₂pz bridging ligand to Pt₂Ag₃(ppy)₂ moiety, LMM'L'CT [Ph₂pz→Pt/Ag/ π^* (ppy)] transition. Optimization of the geometries of triplet excited states revealed that, similarly to the previously reported emission of **2b**,^{3h} 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 [Ph₂pz→Pt/Ag/ π^* (ppy)] excited state. These assignments are fully consistent with the observations that the Pt₂Ag₂ complexes exhibit

structured emission spectra, while the Pt₂Ag₃ 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 Pt₂Ag₂ complex [Pt₂Ag₂(ppy)₂(Ph₂pz)₄] having pre-organized cavity suitable for incorporating Ag(I) ion. The Ag(I) ion trapped in the cavity was stabilized by two dative bonds as well as Ag-C(ipso) bonding interactions from each cyclometalated Pt coordination plane, which regulate the rotation of Pt coordination plane along Pt⊕⊕⊕Pt axis. 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 bond. However, once the Pt₂Ag₃ 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. 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 Pt₂Ag₃ complex. The formation of Pt→Ag dative bonds drastically changes the structured emission spectrum into broad one with altering the emissive state from ³LC excited state to ³LMM'L/CT excited state. Consequently, a reversible formation and cleavage of Pt→Ag dative bonds within the pre-organized cavity of Pt₂Ag₂ complex has successfully been demonstrated. Elucidation of the properties of ground and excited states added new insights into the nature of dative bond.

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- 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).